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ESTIMATION METHODS FOR PROCESS CONSTANTS AND PROPERTIES USED IN FATE ASSESSMENTS

by

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16. ABSTRACT

Physical property data, rate constants, and equilibrium constants are required for assessments of the fate of chemicals in the environment. Structure-activity relationships (SARs), property correlations, and reactivity correlations are sources of such data that are increasingly recognized as rapid, practical, and inexpensive methods with which to estimate values of some constants or properties. Although it is unlikely that major environmental decisions will be made based solely on such information, these estimates are often useful within the context of deciding whether better data are required for an assessment, whether a process may be important for a particular chemical, or as a check on a reported value. In some cases, estimated data are useful in concluding that a chemical will or will not persist in a specific environmental situation by simple analogy to experience with other chemicals having similar properties or reactivities. This report reviews a broad range of qualitative and quantitative relationships between structure and properties or reactivities as well as correlations among different properties and reactivities. Also included are the specific theoretical and enpirical equations used in fate assessments that use data produced by these estimation methods. The limitations of these estimation methods are discussed as are testing procedures.

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FOREWORD

Environmental protection efforts are increasingly directed towards preventing adverse health and ecological effects associated with specific compounds of natural or human origin. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of environmental contaminants, the Technology Development and Applications Branch develops management and engineering tools for assessing or controlling toxic substances in the environment.

For more than 50 years, scientists have attempted to develop relationships between molecular structure and chemical reactivity, molecular properties, and toxicity. In recent years, interest in these structure-activity relationships and property reactivity correlations as applied to environmental assessments has increased, particularly in the evaluation of new chemicals to be introduced into commerce. This report examines the potential of these estimation methodologies to pollutant fate assessment applications and makes recommendations for future development and testing.

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ABSTRACT

Physical property data, rate constants, and equilibrium constants are required for assessments of the fate of chemicals in the environment. Structure-activity relationships (SARs), property correlations, and reactivity correlations are sources of such data that are increasingly recognized as rapid, practical, and inexpensive methods with which to estimate values of some constants or properties. Although it is unlikely that major environmental decisions will be made based solely on such information, these estimated data are often useful within the context of deciding whether a process may be important for a particular chemical, whether better data are required for an assessment, or as a check on a reported value. In some cases, estimated data are useful in concluding that a chemical will or will not persist in a specific environmental situation by simple analogy to experience with other chemicals having similar properties or reactivities.

This report reviews a broad range of qualitative and quantitative relationships between structure and properties or reactivities as well as correlations among different properties and reactivities. Also included are the specific theoretical and empirical equations used in fate assessments that use data produced by these estimation methods. The limitations of these estimation methods are discussed as are testing procedures.

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1. INTRODUCTION

Physical property data, rate constants, and equilibrium constants are required for assessments of the fate of chemicals in the environment. Structure-activity relationships (SARs), property correlations, and reactivity correlations are sources of such data that are increasingly recognized as rapid, practical, and inexpensive methods with which to estimate values of some constants or properties. Although it is unlikely that regulatory or other major decisions will be made based solely on such data, these estimated data are often useful within the context of deciding whether a process may be important for a particular chemical, whether better data are required for an assessment, or as a check on a reported value. In some cases, estimated data are useful in concluding that a chemical will or will not persist in a specific environmental situation by simple analogy to experience with other chemicals with similar properties or reactivity.

The objective of this study was to review the availability and application of structure-activity relationships and property-reactivity correlations that may be used in fate assessments for chemicals in the environment. The limitations and testing of these estimation methods are discussed, and recommendations for future efforts in development, extension, and testing of these methods are made.

1.1 General Definitions

This report reviews a broad range of qualitative and quantitative relationships between structure and properties or reactivity as well as correlations among different properties and reactivities; we have also included the specific theoretical and empirical equations used in fate assessments that utilize data from these estimation methods. For this report, we define SARs as methods by which data or information on the reactivity or properties of a chemical can be inferred or calculated from a knowledge of the structure of a molecule alone. Some SARs have been expressed in a quantitative form as the Hammett equation for estimating rate or equilibrium constants

$$\log \frac{k_X}{k_H} = \sigma\rho \qquad (1.1)$$

where k_X and k_H are the respective constants for chemical structures with a substituent X and a reference substituent (usually hydrogen), ρ is a constant for the reactivity of the chemical, and σ is a constant for the effect of the substituent X on the reaction (for examples see Section 20). Alternatively, SARs may be expressed as additivity relationships

$$\log k = \Sigma n_i f_i \qquad (1.2)$$

$$\log k = \Sigma n_i \alpha_i \beta_i k_o \qquad (1.3)$$

where k is a property or constant, n is the number of times the i-th fragment appears in a molecule, and f_i is a value for the contribution of the fragment to the property or constant of interest [equation (1.2)]; for a rate or equilibrium constant the additivity relationship [equation (1.3)] can include factors $\alpha_i \beta_i$ for the effect of substituents on k_o, which is a rate constant for a reference (or standard) group bearing no substituents (see Section 25 for examples).

Correlations between properties or between reactivities (PRCs) are relations by which one property or reactivity is estimated from another but without a specific concern for molecular structure. One example of a PRC is the correlation of octanol/water partition coefficients, K_{ow}, with K_{oc} values, which are sediment partition coefficients corrected for fraction of organic carbon in the sediment; the form of this equation is shown below, and is discussed more fully in Section 8:

$$\log K_{oc} = (a) \log K_{ow} + b \qquad (1.4)$$

Although PRCs and other estimation equations used in fate assessments do not require specific knowledge of a molecular structure or the use of structural information in the calculations, in many cases the equations do implicitly assume some molecular behavior (e.g., no hydrogen bonding effects, unit activity coefficients), and the correct use and the limitations of the methods may have to include some evaluation of molecular structure (see Section 4.3).

1.2 Scope of this Report

In Sections 2 and 3 we present our conclusions and recommendations based on the methods evaluated in this report. Section 4 of this report discusses general aspects of the source, applications, and limitations of estimation methods in fate assessments. Section 5 through 27 of this report describe the methods currently available for estimating property data, rate constants, and equilibrium constants for use in environmental assessments. The survey for SARs, PRCs and other estimation methods were limited to the properties or constants that may be used in the EXAMS fate model; these are listed in Table 1.1. The methods discussed in this report may, of course, be used for other assessments providing the processes are described in the same way. (Although SARs have been used extensively for estimating toxicity, they have not been included in the scope of this report.) For each property or constant a brief statement is provided on how the property or constant is used in fate models or otherwise is used in SARs or PRCs to estimate data for use in fate models. The methods available for estimating the particular constant or property are then discussed. SARs for environmental processes have been reviewed previously, notably by Hendry and Kenley (1979) (for air chemistry), by Mill (1979), and by Lyman et al. (1982); the latter has resulted in a published handbook of estimation methods. This report incorporates some of that information as well as recent results from this laboratory, the open literature, and discussions with persons active in the relevant areas of research. In some cases this report evaluates or compares the various SAR methods, and comments on their current use and the limitations.

For each constant or property, we compare the practicality and limitations of each method for estimating data to be used in fate assessment models. We also provide recommendations for future efforts in developing or expanding the method. Because the data base used to establish the method is often important in understanding the scope and limitations of an estimation method, some comment on the quality and size of the data base is provided when relevant.

In a few cases, our review found that more than one SAR or PRC was available for a particular property or constant, and we have conducted or recommended a critical evaluation of the methods rather than further development. In cases where quantitative SARs are not available, some possible formats for listing information as SAR data bases or as qualitative SARs are suggested; these formats are designed to be easily included in a computerized SAR system that can be used by a reasonably knowledgable environmental scientist or engineer. The SARs, PRCs, and estimation methods are discussed in the context of a tiered assessment methodology in recognition of the fact that it is often practical and cost effective to first identify the most important transformation and transport processes a chemical may undergo, then use more accurate and precise methods to estimate data for the important processes.

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Hendry, D. G., and R. A. Kenley. 1979. Atmospheric Reaction Products of Organic Compounds. EPA Final Report. EPA 560/12-79-001.

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York.

Mill, T. 1979. Structure Reactivity Correlations for Environmental Reactions. EPA Final Report. EPA 560/11-79-012.

Table 1.1

PROPERTIES AND CONSTANTS USED IN FATE ASSESSMENT

Property or Constant	Abbreviation
Molecular weight	MW
Octanol/water partition coefficient	K_{ow}
Sediment partition coefficient	K_p
Sediment partition coefficient, normalized for fraction organic carbon	K_{oc}
Melting point	MP
Solubility in water	S_w
Boiling point	BP
Heat of vaporization	ΔH_{vap}
Vapor pressure	P_v
Henry's constant	H_c
Diffusion coefficients in liquid phase and gas phase	D_ℓ, D_g
Reaeration rate ratio	k_v/k_o
Volatilization rate constant	k_v
Dissociation constant	K_A, K_B
First-order hydrolysis rate constant	k_h
Acid-promoted hydrolysis rate constant	k_A
Base-promoted hydrolysis rate constant	k_B
Neutral hydrolysis rate constant	k_N
Direct photolysis rate constant	k_p
Reaction quantum yield	ϕ
Light absorption coefficients	ε_λ
Oxidation rate constants	k_{ox}
Second-order biodegradation rate constant	k_b

2. CONCLUSIONS

Structure activity relationships (SARs) and property reactivity correlations (PRCs) are cost-effective and rapid methods for estimating data for use in some fate assessments. Estimation methods are currently applicable to many chemicals for estimating sediment sorption partition coefficients and rate constants for volatilization, hydrolysis, and oxidation; direct photolysis and biotransformation are complex processes for which no general and accurate estimation methods are available, but some rules for evaluating the possible importance of these processes are available. Some SARs are limited to prediction of limiting (i.e., maximum or minimum) rate constants and are very useful in screening level assessments for decisions of whether or not to include a process in subsequent and more detailed assessments.

Selection and application of SARs requires varying degrees of expertise that depend on the structure of a particular chemical of interest, knowledge of the mechanism of the process, the extent of the data base used to develop the SAR, and the complexity of the structural analysis required to relate structure to the property or constant. All SAR methods are empirical correlations of molecular structure parameters and reaction or property constants and are based on approaches that use molecular fragment additivity methods as well as methods that use empirical parameters that represent specific structural influences (e.g., steric, polar, or resonance effects). PRCs also are simple methods for estimating properties or constants using values for related properties or constants and require expertise similar to that necessary for the application of SARs. Although PRCs can, in principle, be replaced by SARs (i.e., calculation of properties or constants directly from structure), many PRCs are simple and accurate methods that make some SARs unnecessary.

Current environmental assessment efforts within (EPA) have found that estimation methods are useful, and in many cases, the only source of data. Some computerization of these methods has been begun by EPA-OPTS, and further development and testing of SARs and PRCs and computerization of these methods promises to provide a consistent and reliable source of data for future assessments.

Below we summarize the utility of these SAR's as screening tools for EPA's fate and hazard assessments of new and old chemicals. We have used two formats to show the existing gaps in SARs and also where we now can use SARs with a high degree of confidence in their reliability and accuracy. Both formats are necessary because no one format easily lends itself to illustrating both strengths and deficiencies in the SARs now available and whether more development is needed to improve or extend them.

First, in Table 2.1 we list properties and rate constants for which estimation methods are now available; we indicate the state of development, limitations and need for additional work to improve existing SARs or develop new ones. Second, in Tables 2.2-2.6 we crosslist for each transformation process (hydrolysis, oxidation in air, oxidation in water, photolysis and biotransformation) major classes of organic functional groups which react by that process and our judgement of the overall utility of applicable SARs.

The utility of a SAR can be judged on the basis of four criteria: process, scope, statistics and reliability. Process refers to the degree of understanding we have of the molecular events (bond-making and bond-breaking or molecular movement) which the SAR describes. Knowledge of these events provides the user a more reliable basis for applying the SAR to a new molecule. Scope refers to the breadth of structural variations used in development of the SAR; a wide range of structures is more likely to give a SAR which is applicable to a new structure. Statistics refers to overall precision of an estimate as well as the precision of the SAR parameters themselves. Reliability is a measure of how often, in x estimates, an estimation method will predict a correct result within some predetermined range or limit.

Table 2.1

STATUS AND NEEDS OF SAR'S

Chemical Property	Status	Needs
P_v BP	Estimations poor	Evaluation of available data for new or improved methods.
H_{vap}	P_v vs T correlations difficult for $P_v < 1$ torr	Develop P_v vs T for class specific correlations.
MP	Easily measured	-
MW	Easily calculated	-
Solution Property		
K_{ow}	Several correlations available	Thorough analysis of accuracy of estimating K_{ow}.
S_w	Requires good K_{ow} data	Expand data base for K_{ow}/S_w.
K_p K_{oc}	Estimation methods good where van der Waals forces dominate	More data using standardized sediments. More information and data on sorption due to ion-exchange, and complexation processes.
H_c	Estimation good for low solubility chemicals	Requires P and S_w data.
D_ℓ, D_g	Good estimation methods available	No work needed.
k_{vc}	Estimations good for high volatility chemicals	More work required on low to intermediate volatility chemicals.

Table 2.1 concluded

Transformation Constant	Status	Needs
k_h	Requires knowledge of k_A, k_B, and k_N	-
k_A	Good to poor, depending on class of chemicals	Fill data gaps to extend SAR; k_A for some classes not known
k_B	Excellent to poor depending on class of chemicals	Fill data gaps to extend SARs
k_N	Poor, unless hydrolysis pH independent	Reliable data in water solvent and mechanism/ process studies
k_{pE}	Requires knowledge of ϕ and ε_λ	-
ϕ	Poor; limiting values by assuming $\phi = 1$	Reliable data in water solvent; mechanism studies also necessary
ε_λ	Poor; easily measured in most cases	Reliable data in water solvent.
k_{ox}	Excellent to fair, limiting values estimateable for most organic chemicals	Some selected data gaps need measurements.
k_{BIO}	Poor	Better fundamental understanding of process; reliable data base organized according to reaction class.

Table 2.2

SAR Utility Index for Hydrolysis[a]

Classes of Chemicals Which Hydrolyze	k_A	k_B	k_N	Comments
Halides		G	G	Not quantitative
Esters	F	G	P	Small data base for k_N, limited data for k_A
Amides	G	G	P	
Epoxides	G	P	G	k_B usually not important
Phosphorus Esters	P	G	G	k_A usually not important
Haloesters	P	P	F	No data for k_A or k_B
Carbamates				
O-Aromatic	F	G	F	k_A usually not important;
O-Aliphatic	P	G	P	k_N may be dominant

---

[a] E,G,F,P: excellent, good, fair, poor.

Table 2.3

SAR Utility Index for Oxidation by HO[a]

Classes of Chemicals Which Oxidize with HO[b]	Utility k_{HO}[c,d]	Comments
Alkanes	E	
Alkenes	G	
Oxyalkanes[e]	G	Ketones have poor utility
Acids and Derivatives	P	Poor data base
Haloalkanes	F	
Haloalkenes	F	
Aromatics	E	Good correlations using σ^* values
Sulfur Compounds[f]	P	No data base
Amines	P	No data base

---

[a] Refers to abstraction, addition, and O-atom transfer.
[b] All classes oxidize except perhaloalkanes and perhaloketones.
[c] E, G, F,P; excellent, good, fair, poor.
[d] Utility is overall usefulness for fate assessment; see text.
[e] Includes alcohols, ethers, carbonyl's.
[f] Includes sulfides, thiols and disulfides.

Table 2.4

SAR Utility Index for Oxidants in Water[a]

Classes of Chemicals Which Oxidize[b]	Utility[c]	Comments
Alkanes	E	High reliability; reactions slow
Alkenes	E	Same as alkanes
Oxyalkanes[d]	G	Limited data base
Aldehydes, ketones	F, G	Limited data base
Halocompounds	F	Limited data base; usually slow reactions.
Sulfur Compounds[e]	G	Reactions fast
Amines and Hydrazines	F,G	
Aromatics	.G	Reactions very slow
Phenols	E	Reactions fast
Heterocycles	P	Limited data base

---

[a] Oxidants are RO_2, $^1O_2$ and triplet diradicals.

[b] Most classes will oxidize with one or more oxidants except perhalo compounds and carboxyl derivatives.

[c] E, G, F, P: excellent, good, fair, poor.

[d] Includes ethers and alcohols.

[e] Includes thiols and sulfides.

Table 2.5

SAR Utility Index for Direct Photolysis[a,b]

Classes of Chemicals Which Photolyze[b]	ϕ_r[c]	Comments
Aromatics[d]	F	Large range of ϕ_r values, crude relation to mw.
Nitroaromatics	F	Wide range of nitrobenzenes and ϕ_r values.
Chloroaromatics[e]	F	Data base in organic solvents; ortho-Cl high ϕ_r; p-Cl, low ϕ_r.
Ketones, Aldehydes	P	Few data in water; mechanisms well understood but complex.
Heterocycles[f]	P-F	Some data in water for benzo-substituted furans, thiophene and N-rings.

---

[a] Few SARs are available for direct photolysis; these evaluations reflect how well we can generalize about ϕ_r values and/or the availability of data bases: F, P=fair, poor.

[b] This listing includes only classes which absorb light >290 nm.

[c] Quantum yield for reaction.

[d] Unsubstituted polycyclic aromatics.

[e] Includes chlorobenzenes, biphenyls and biphenylethers.

[f] Includes N, S, O-rings and multiple heteroatom substituents.

Table 2.6

SAR Utility Index for Biotransformation[a]

Classes of Chemicals[b]	Utility[c]	Comments
n-Alkanes, Alkenes	G	Rapid
Branch-Alkanes and Alkenes	F	Slow
Halogenated alkanes and alkenes	G	Very slow
Aromatics	F	Slow
Esters	F	Fast
Heterocycles	P	Poor data base

---

[a] No biotransformation SARs are available; these evaluations refer to useful generalizations which might be made based on experience.

[b] Rates of biotransformation are particularly sensitive to structural features in the molecule.

[c] E, G, F, P: excellent, good, fair, poor.

Reliability is important in environmental assessment because if the value of an estimated rate constant is very small or very large (range) the true value (accuracy) no longer is very important, especially for screening purposes. Chemicals which move or transform very rapidly ($t_{1/2} < 1$ hr) or very slowly ($t_{1/2} > 10$ yr) pose very different potential hazards than those which transform with a half life in the range of a few hours or a few months. Thus screening assessments for very reactive or unreactive chemicals usually do not need very accurate or precise values but do need reliable estimates of the limiting values.

Neither direct photolysis nor biotransformation generally are sufficiently well-understood to provide quantitative SARs; Tables 2.5 and 2.6 are included because data bases for these processes are available and in some cases are quite extensive (e.g., photolysis of aromatics). Useful generalizations are possible in many cases even though estimation of process constants for specific chemical structures may be quite inaccurate and imprecise.

3. RECOMMENDATIONS

The various estimation methods require different levels of effort in their development, extension, and testing to provide data of known accuracy and precision for use in fate assessments. Recommendations are presented below for priorities of these efforts for the individual environmental processes. A major effort should be directed to incorporate estimation methods in computer systems to provide rapid and consistent use of SARs and PRCs, which experts may then review and apply correction factors, when necessary.

Sorption to Sediments. The correlation of octanol/water partition coefficient, K_{ow}, with K_{oc}, the sediment partition coefficient normalized for organic content, needs to be tested using quality K_{oc} data; as these data are obtained, development of more accurate correlations for specific classes of chemicals should be possible. Basic research on the sorption of polar and ionic chemicals to sediments is required to determine the limitations of the K_{ow}/K_{oc} correlations and potentially to develop SARs/PRCs for these other sorption processes to better estimate the total sediment partition coefficient.

Volatilization. The equation used to estimate volatilization rate constants should be tested in the laboratory and under field conditions for chemicals with high and low Henry's constants. If an accurate set of Henry's constants, water solubility, and vapor pressures are obtained, the accuracy and error propagation in estimating these properties from established SARs and PRCs should be tested. The accuracy of methods used to estimate diffusion coefficients are adequate for environmental assessments, and therefore further development or testing of these methods is not recommended.

Hydrolysis. Although SARs for hydrolysis of major classes of hydrolyzable chemicals are available, more qualitative and quantitative SARs should be developed for estimating rate constants for acid-promoted, base-promoted, and neutral hydrolysis processes for other classes of chemicals. These efforts will require some laboratory measurements to extend the SARs to a broader range of structures and also to test the SARs. The qualitative and quantitative hydrolysis SARs that are available should be incorporated in a computerized system to demonstrate the feasibility of an SAR system that extends from a structure-search routine to actual estimation of a rate constant.

Direct Photolysis. The ability to predict a direct photolysis rate constant depends on obtaining a reaction quantum yield and the absorption spectrum of a chemical. No methods are currently available for estimating absorption spectral data, and we recommend that methods for estimating these data be explored. The ability to estimate a reliable reaction quantum yield will depend on a more complete understanding of structural influence on the various mechanisms of photolysis and the competing processes (energy transfer, deactivation), which complicate the evaluation process. In addition to obtaining accurate data for reaction quantum yields (measured in water solvent) from which some useful generalization may be made, we recommend that studies be designed and undertaken to develop a theoretical framework on which the chemistry of photoexcited states may be evaluated.

Oxidation. SARs for estimating oxidation rate constants for several oxidants in water are available, but we recommend that SARs for HO• oxidation in air be extended to a wider range of structure. Computerization and limited testing of oxidation SARs should be done.

Biotransformation. The ability to estimate biodegradation rate constants that can be used in environmental assessments requires an understanding of fundamental processes that control biodegradation rates. Successful development of SARs requires that one type of reaction process be studied (e.g., biologically mediated hydrolysis or oxidation). Recent studies have shown that sorption-related processes also may be important in determining biotransformation rates. Measurement of relative rate constants for chemicals under identical experimental conditions and correlation with molecular properties or reactivity is probably the most cost-effective way of developing biotransformation SARs.

4 ROLE OF ESTIMATION METHODS IN FATE ASSESSMENTS

4.1 Basis for Estimation Methods

Attempts to develop relationships between molecular structure and chemical reactivity, molecular properties, and toxicity have been a major effort of scientists for more than a half-century. Such knowledge will not only allow for a better understanding of the chemical and biological processes, but may also allow science to protect and improve the quality of life. Indeed, SARs have been successfully used in the design of drugs for many years (Martin, 1978). Although Wiberg (1964) has candidly noted that SARs have been used more to understand the mechanisms of chemical reactions rather than to predict rate constants or molecular properties, a thorough understanding of the mechanism of a process and the factors determining a particular property are essential for the correct use of SARs or PRCs and for recognizing their limitations and inappropriate applications.

Although it would be desirable to reduce all relationships between molecular structure and properties or reactivity to quantitative relationships, the understanding of many of these processes and relationships is incomplete. However, what is known about a process or property should not be ignored because a quantitative relationship between a structure and property or reactivity is lacking. The importance of qualitative information has been recognized by L. P. Hammett (1974), one of the pioneers of structure-activity relationships, who noted that "chemists had arrived empirically at effective working principles long before the theoretical key to all the problems of chemistry was embodied in the Schrodinger equation of wave mechanics. Even today, the amount of information which the chemist can derive directly from that equation is only a small part of what he knows." Thus, in the development of SARs for use in environmental assessments and in the consideration of SARs that may be made available in a computerized SAR system, both qualitative and quantative relationships should be included. As part of an SAR system, data bases also can serve as a basis for developing quantitative relationships when more data become available or insight on the process is developed.

Even a cursory review of the chemical literature shows that many different types and forms of SARs and PRCs exist for estimating properties, rate constants, and equilibrium constants. Some SARs and PCR are broader than others in the range of chemicals that are covered, and some methods have been established with a better understanding of the mechanisms or properties involved. Although a unified characterization of structural effects on properties and reactivity may be a desirable basic goal in the application of SARs, historical development of SARs and PRCs has been by independent and fragmented efforts. Again, we quote Hammett (1974) in his discussion of a unifying approach to SARs in physical organic chemistry: "For this, as for any other human attempt to master nature, two kinds of approaches are possible. One is the construction of broad, far-reaching principles from which the detailed properties of matter can be deduced. The other involves the bit-by-bit development of empirical generalizations, aided by theories of approximate or limited validity whenever they seem either to rationalize a useful empirical conclusion or to suggest interesting lines of experimental investigation. By the nature of our material we chemists are forced to depend on the second pathway." This situation applies equally well to the development and use of SARs, PRCs, and other estimation methods in environmental science. Thus a practical approach is to pursue the "bit-by-bit development" approach to obtain fundamental data that can be used to at least develop operational relationships, with the hope that as chemical theory develops more unifying concepts, a common approach for one SAR system will be possible.

In considering the particular approaches used for SARs in conjunction with fate assessments, it is important to recognize that properties and constants used for evaluating the transport of chemicals in the environment are collective; that is, all molecular parameters contribute to the property or constant. These parameters may be related to molecular weight, elemental composition, spatial relationships, and the size of the molecule. Transformation processes, on the other hand, are usually evaluated in terms of functional groups that undergo bond changes by specific mechanisms; the rates of these chemicals and biological reactions are usually affected only by substituents one or two atoms removed from the reaction center. These substituents act on reaction sites through chemical bonds (e.g., resonance or inductive effects) and/or through space (steric or polar effects) (Detar, 1980). The fundamentally different nature of the transformation and transport processes and their associated constants and properties requires different types of analyses and treatments of molecular structure and often different levels and types of statistical analyses. Thus, simple regression analysis of measured rate constants (actually log k_X) against σ values may be adequate for determining a ρ value for the Hammett equation [equation (1.1)], whereas a more complex multivariate analysis may be required for a fragment additivity SAR in which multiple values of f_i may have to be determined from a number of k values [equations (1.2) and (1.3)].

4.2 Application of Estimation Methods in Fate Assessments

As part of the regulatory mission of EPA, various program offices must make decisions on whether or not a chemical presents a hazard to human health or the environment. One of the issues in the decision process is the environmental fate of the chemical: where will the chemical go in the environment, how long will it persist, and what are the transformation products? These questions are not new for EPA staff, who usually have been able to make decisions based on information from industry and literature as well as utilizing expertise within EPA and available from EPA contractors. However, under provisions of the Toxic Substances Control Act of 1976, EPA must review any new chemical as part of a premanufacture notice (PMN) procedure to determine whether or not production of the chemical may pose a hazard. This review must be accomplished quickly and usually with few data initially supplied by the manufacturer. Because numerous chemicals are being submitted for review, SARs and PRCs are important sources of data for initial evaluations of these new chemicals.

To answer questions about the fate of a chemical in the environment, EPA needs data on rate and equilibrium constants for a variety of processes that control the fate of the chemical in water, soil, and air; these processes include volatilization, sorption, oxidation, hydrolysis, photolysis, and biotransformation. In the absence of measured values for the process or property constants, EPA scientists must use their professional expertise and judgement to estimate these constants. Much of the expertise used is based on extensive measurements on similar chemicals that have been codified as SARs or PRCs. When properly applied, these methods are powerful tools for estimating rate or equilibrium constants or properties. In some cases they may be useful only for providing upper or lower bounds on values for the processes; nevertheless, this information is often very valuable.

Because SARs and PRCs require no specific laboratory measurements, some individuals regard the estimation methodology as the only one needed for fate assessments at the screening levels. Others regard these methods as suitable only for the most preliminary screening level decisions, and then with limitations. However, it is clear that SARs and PRCs must and will be used by EPA in situations such as the PMN review simply because there are no suitable alternatives. For this reason, it is important to know how best to use the estimation methods to take advantage of their accuracy and utility while avoiding serious misapplications that will undermine the whole assessment procedure.

The use of SARs and PRCs in EPA activities gives rise to several questions that also are relevant to other fate assessment applications:

- Can estimation methods alone be used for decision making or should SARs be used only to trigger laboratory measurements of needed data?
- Are qualitative SARs useful in modeling and decision making or should their use be restricted to preliminary screening efforts?

- What are the criteria that should be used to judge whether SARs and PRCs may be used without susbstantiation by laboratory measurements?

No single or simple answers to these questions will cover all situations, but the questions do provide a useful framework in which to discuss the process-specific SARs in subsequent sections of this report.

In addition to the scientific issue involved in these questions, policy decisions on whether such indirect methods are acceptable may be required. An example of such a decision is the use of an SAR that consistently predicts greater persistence than is actually found; such an SAR would be acceptable for conservative methodology, but may trigger unnecessary detailed studies (i.e. give false positive hazard assessments).

In considering the use of an estimation method in a fate assessment methodology, a logical question may be posed: "How reliable is this method?" Careful analysis of this question reveals that two questions are actually involved:

(1) Can the method provide an accurate and precise estimate.

(2) Is the value accurate enough to be useful within the context of a particular assessment?

Thus, the reliability of a value obtained with an SAR or PRC is in part defined by how it is used. In many cases, as exemplified by the PMN process, the estimation method may be the only source of a process constant. If an estimated value is used in an assessment, and the process is found to be important compared to other processes, careful analysis of the entire assessment is then required to determine the accuracy and precision of the estimation method as well as sources of uncertainty in the use of the value. Thus, a two-fold uncertainty in an acid- or base-promoted hydrolysis rate constant may be moot if the pH of a water body cannot be specified to within one pH unit, which can be a factor of 10 in the first order rate constant for a pH dependent hydrolysis reaction. Indeed, careful examination of the discussions regarding the reliability of SARs and PRCs may show that it is the use of the values that is at issue, not the methods themselves.

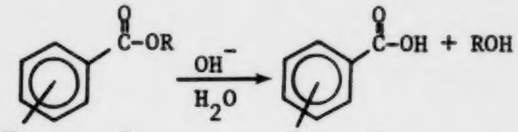
Estimation methods are available for both equilibrium (time-independent) processes and kinetic (time-dependent) processes, and some estimation methods require data obtained from other SARs or PRCs. For example, knowledge of the octanol/water partition coefficient, K_{ow}, of a nonelectrolyte chemical can be used to estimate the water solubility, S_w, of the chemical from an correlation equation of the form (see Section 10).

$$\log S_w = (n) \log K_{ow} + C \tag{2.1}$$

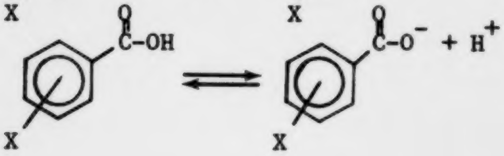
The value of K_{ow} itself may be obtained by one of several measurement methods or by calculation using an SAR method such as the FRAGMENT approach of Leo and Hansch (1979). In another application of SARs, knowledge of the equilibrium constant (K_A) for ionization of an aromatic acid can be used to estimate a rate constant for OH-promoted hydrolysis (k_B) of the aromatic acid ester

$$\log k_B = \rho \log K_A \tag{2.2}$$

where k_B is for the reaction



and K_A is for the equilibrium



This is an example of how a kinetic constant can be used to estimate an equilibrium constant if the structures undergoing the different processes can be related; the value of k_B may be obtained by direct measurement or by another SAR or PRC.

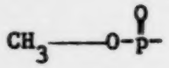
In the above examples, neither equation contains explict information about a particular chemical structure, although some information about chemical structure is implict in the parameters n, C or ρ. Estimation of S_w does require the ability to recognize that a chemical is a nonelectrolyte, and estimation of log K requires recognition of common features for the aromatic acid/ester structures. Thus the proper application of the SARs and PRCs requires that the user understand the limitations and range of applicability of each equation, that is, what kinds of chemical structures are encompassed by the respective equations. The recognition and sources of limitations in the use of estimation methods are discussed in the following section.

Perhaps the greatest difficulty encountered in applying SARs or PRCs to a specific estimation procedure is the choice of the correct equation, rule, or correlation that relates a specific chemical structure to a process or property of interest. In estimating transformation rate constants, for each process (e.g., hydrolysis or oxidation) discrete reactants, pathways, and intermediates describe specific mechanistic channels and to each a specific SAR applies. The cardinal rule for using SARs is that all chemical structures that adhere to a specific SAR must share the common pathway.

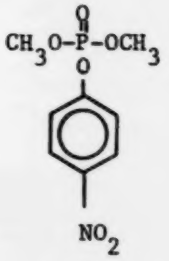
For example, p-nitrophenyl dimethyl phosphate, I, is a molecule that in principle can hydrolyze, photolyze, and oxidize. Are there SARs that can be used to estimate rate constants for these reactions, and, if so, how does one select the correct SAR? The first step in this analysis is to dissect the structure into subunits that we recognize can react by specific processes. The following example illustrates the identification of specific reaction centers for which specific SARs apply.

Hydrolysis* $-\mathrm{P(O)}$——$\mathrm{OCH_3}$

$-\mathrm{P(O)}$——$\mathrm{C_6H_4NO_2}$



$\mathrm{CH_3}$——$\mathrm{O{-}\overset{O}{\overset{\|}{P}}{-}}$



I

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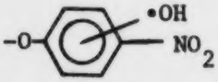
*Bond undergoing reaction is lengthened.

Photolysis* -P(O)——$C_6H_4NO_2$

-P(O)-$C_6H_4N(O)$——O

Oxidation* H——CH_2- (H atom transfer)



(addition of •OH to ring)

For each process, there are several possible different pathways for reaction:

Hydrolysis: Acid promoted; base promoted; neutral hydrolysis.

Photolysis: Photonucleophilic substitution by water or base; photodissociation of N-O bond.

Oxidation: H-atom transfer by RO_2; OH addition to aromatic ring. Each pathway and structural subunit form a unique pair for which a specific SAR may be applicable; for example:

-P(O)——OCH_3 by nucleophilic displacement with OH^-

-P(O)——OCH_3 by solvolysis (water is reactant)

-CH_2——H H-atom transfer by •OH

Analysis of structure also is required for estimating data for predicting the volatilization rates of a chemicals in an environment, although the analysis is different and sometimes simpler since the total molecular structure must be considered in estimating the collective properties of the diffusion coefficients in air and water and Henry's constant. Sorption to sediment or biota also is readily predicted if a K_{ow} value is available or can be calculated by any one of several methods and if it is assumed that sorption is dominated by hydrophobic phenomena.

The foregoing analyses illustrate the need for expertise and judgement in applying SARs and PRCs to fate assessments. Much of the expertise needed can be formalized as rules for applying SARs and put into computerized format for use by nonexperts. Such a system would not only expedite the estimation process, but would also free experts for the more detailed aspects in the PMN review. However, the values derived from the estimation procedures have a wide range of accuracy, precision, and reliability that are important in their usefulness for a particular assessment.* Low accuracy and reliability sometimes occur because some pathways are poorly understood or no simple or quantitative estimation method exists for estimating the property or constant.

In some cases very reliable but only qualitative SARs exist that may be useful at a screening level, where only limiting or qualitative estimates often are all that is needed to decide whether or not a specific process will be important. An example is the hydrolysis of unsubstituted amides by acid- or base-catalyzed processes. Data available for these processes place half-lives for these reactions at over 100 years at pH 7 and 25°C (Mabey and Mill, 1978). Thus it is clear that hydrolysis processes need not be considered further nor are any measurements required. At this level of use of data, the precision of the value is not important because a half-life of 10, 100, or 1000 years leads to the same conclusion; what is important is that the accuracy of the boundary value be correct. In other circumstances precision and accuracy are important for the reliable use of data, as when comparing process constants of comparable magnitude or when conducting sensitivity analyses.

4.3 Limitations of Estimation Methods

The proper development and use of estimation methods requires that the mechanism or factors controlling a property or reaction be understood; it follows that any limitations of methods must be clearly included with the SAR or PRC and must be understood by the user of the method. These limitations are best understood by those who develop the method and who must explain these limitations as completely as possible. Of course, it is impossible to anticipate every way in which a method may be applied, and therefore the user must bear the ultimate responsibility for consulting persons with appropriate expertise if any questions arise about the use of a method for a specific chemical. As part of the estimation procedure, all calculations, assumptions, and rationale for selecting methods should be recorded so that an independent and critical review of the estimation procedure can be conducted if necessary.

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*By precision we mean the error bound about the estimated value; by accuracy we mean the closeness of the estimated value to the true value; by reliability we mean the probability that the method will give values in a stated range that are useful in an assessment.

Evaluations of the limitations of an SAR or PRC first should determine what assumptions are explicit or possibly implicit in the method. For example, the relationship between S_w and K_{ow} [equation (4.1)] is based on hydrophobic behavior of nonelectrolytes; in another case, a qualitative SAR for hydrolysis of alkyl halides may not discriminate between several possible mechanisms but still will accurately reflect variations in rate constants with structure. After these important evaluations, the method may then be examined for its accuracy in predicting a property or constant; if the SAR or PRC is a quantitative relationship, the statistical analysis of the data can also be useful in ascertaining further limitations of the method.

Although the limitations and assumptions for specific SARs and PRCs are discussed in other sections of this report, it is useful to review the general limitations of the SAR or PRC approach. In considering the limitations of quantitative estimation methods, it should be recognized that estimated values will seldom match exactly the original values used to develop the SAR or PRC, and the user should examine the statistical analysis to determine how well the estimation method actually correlates the original data. Furthermore, statistical analysis of error propagation is important for knowing the error limits (e.g., standard error, correlation coefficients) that bound any calculated value.

In the specific case of the limitations of SARs, one reason why estimated and original values do not match is that (in addition to the experimental error) significant error can be introduced into the development as well as the application of an SAR due to an unrecognized change in the importance of different structural effects among a group of chemicals that are considered related; neglect of such changes will adversely affect precision in the development of an SAR or may result in inaccurate estimates if not recognized in the application of the SAR. For example, an SAR that relates structural variations in a molecule to a rate constant in terms of steric effects can be accurately applied if electronic effects are not important, or are at least constant for a group of related chemicals. If, in the application of the SAR to a new chemical, structural modifications change the electronic substituent effect but to a lesser degree than they change the still-dominant steric effect, the SAR may still be successfully used but with some loss of accuracy. If structural changes result in large changes in electronic effects compared to steric effects, the application of the SAR will provide highly inaccurate rate constant estimates.

From this example, we see that having a wide range of structural features represented in a data base is important for evaluating the accuracy of an SAR as it is applied to a particular structure. Comparison of the structural features encompassed by the data base and those of a chemical of interest may show that (1) no significant differences exist, (2) the structural differences are significant and the method is not applicable, or (3) the chemical has structural features not contained in the data base, but the differences do not affect the mechanism of the process being evaluated. In practice, the nonexpert user of an SAR may recognize that a chemical belongs in one of the first two categories, but some expertise may be required to decide whether a chemical actually belongs in the last category. If an SAR is applied to a chemical structure that lies outside the data base, the estimated value should be carefully identified as being obtained from an extrapolative use of the method (i.e., outside of the data base) and be a candidate for immediate review after initial evaluation of data.

Limitations in the use of PRCs are similar in some ways to those of

SARs in that any assumptions in the development of the method must be recognized, the precision and error propagation can be evaluated, and the data base determines the range of values over which the correlation can accurately be used. However, PRCs are different from SARs in other ways, notably in that no specific analysis of structure is required. In some cases, this situation could lead to the misuse of a PRC by a non-expert because it may appear that one property can be easily calculated from another, whereas examination of structure would show that the correlation should not exist. Thus, the decision of whether a PRC should or should not be used is sometimes a difficult one.

An example of decisions in evaluating the limitations of a PRC is the estimation of vapor pressure data (P_v) from boiling point data (BP), where Mackay et al. (1982) have recently reported that the vapor pressure of a chemical is highly correlated with its boiling point for many hydrocarbons and halogenated hydrocarbons of both aliphatic and aromatic structures. However, when the Mackay correlation was applied to other chemicals with oxygen, nitrogen, and sulfur substituents, the agreement between measured and estimated values was good to poor. Although application of the correlation to these latter classes of chemicals is not strictly correct, its application may suffice to provide estimates that are accurate enough for some assessment purposes. Indeed, careful analysis of the basis for the correlation shows that the key assumption regarding the temperature dependence of the heat of vaporization may hold for chemicals other than those in the two classes used to establish the relationship, and therefore Mackay's correlation between P_v and BP may be more general than it is represented. The correct extension of this correlation to other classes of chemicals should then determine whether the heat of vaporization criteria are met.

In evaluating the limitations of estimation methods, it is also important to recognize that some relationships or correlations are better understood than others and that the size of the data base as well as the structural variations in the data base contribute to the confidence with which a method is used. In some cases more than one method is available because different data bases were used, or a different approach was taken, or simply an evolutionary process in the development of the method occurred. In other cases the SAR is limited by the methods and complexity associated with the ability to dissect a chemical structure in a way that is consistent with the original development of the method, or in having structural fragment values or constants that are tentative because of meager or questionable data. Although many methods can be used by nonexperts, it is likely that SARs and probably many PRCs are more accurately used by persons with more expertise or training in chemistry. Even experts are limited by lack of understanding of a process or property; indeed, many estimation methods are under continual revision as better understanding or larger data bases become available. One example of such a change is the recent addition of a correction factor in the calculation of K_{ow} values of polyhalogenated aromatics, where previously the calculation had considered such structures as simply a summation of the monochlorinated fragments. An example of how the understanding of a process may change an estimation is the report by Karickhoff et al. (1979) that the fraction of organic carbon on a sediment increased with smaller particulate size, and therefore that K_{oc} values calculated from unsized sediments may vary for reasons independent of the chemical used. This realization has led to a better ability to predict accurate K_{oc} values that can be used in fate assessments. From this discussion we see that although SARs and PRCs are practical means from which to obtain data for use in assessments, some knowledge and caution must be exercised in their use.

4.4 Testing the Accuracy of SARs and PRCs

Because SARs and PRCs are practical approaches for obtaining data, it is important to determine how reliable, accurate, and precise these methods may be. However, in testing an SAR or PRC, it is important to remember that there are numerous structures to which an estimation method may be applied and that while the successful testing of a method with one or several different chemicals certainly adds confidence to use of the method, no estimation method can ever be used without some possibility of error being incurred even if it is used by an expert.

The accuracy of a SAR or PRC in predicting a value may be tested in several ways. If a large data base is available for establishing a method, the SAR or PRC may be obtained with part of the data, and the rest of the data can be used to test the method. For such an effort, the testing of a method can easily become a matter of choice and judgement, with conclusions as to the the precision of the method and the testing results being different depending on what sets of data are selected for development of the relationship or testing of the relationship. Independent testing of an established SAR or PRC also involves choosing a test chemical. The structural features of the test chemical may be chosen from within the data base (which may optimize the chances for a successful test) or from features outside the data base. The latter approach is probably the most useful because since it tests the accuracy of the method when used in an extrapolative sense, and, if the accuracy is found to be acceptable, the method in effect has been expanded in its range. Several ways of comparing measured and estimated data to determine if they agree are discussed in the next paragraph. If the values from the two sources do not agree, it is important to examine why disagreement occurred. Among possible explanations are the following:

(1) The SAR or PRC is based on a poorly understood process or property and the method is then of limited or no use.

(2) The measured value is incorrect.

(3) The chemical structure used as the test has features which affect the property or constant but were not included in the original data set.

(4) The structural differences in the test chemical produce an independent competing process which masks the process intended for study.

The criteria for determining whether an estimated value and an independently measured value agree may be formulated in several ways. A simple way is to establish criteria in a use context in which agreement within a certain factor (say 5) is considered acceptable for application. If many independently measured values are available, the average of the differences between the estimated and measured values can be used to represent how well the estimated and measured values agree. Both of these criteria can be misleading however, because they are based on experience with a specific data set rather than on a statistical rationale, and they ignore that each estimated value is an independent "event" (i.e., each calculation uses a different combination of structural features that make it unique from other calculations).

Mill et al. (1982) have discussed comparison of measured and estimated values for reaction rate constants in terms of the precision of each value and recognize that each precision value has a different source. The precision of an estimated value is based on the statistical fit of the structural parameter constants against rate constants, whereas the precision of the measured value is based on a fit of the log of concentration function against time to get the individual rate constant. Because the error in each measured rate constant will be propagated into the SAR or PRC and then into the estimated value, the largest error will probably be associated with the estimated value obtained from the SAR. One statistical approach for assessing agreement is to determine whether the confidence intervals (CI) for each value bound the other value. If the CIs of each value do not overlap the other's CI, the values can be considered to disagree. If the CIs do not overlap but do not bound each others, then further analysis of the data may be necessary. Mill et al. (1982) also discuss a more rigorous statistical analysis procedure for comparing data in a more quantitative manner.

The foregoing discussion illustrates the complex decisions which need to be made to use estimation methods for fate assessments with confidence in the results. In the screening stages of an assessment that assures some typical environmental conditions, very crude estimations of properties, rate constants, and equilibrium constants can be used because the screen is designed only to separate those processes that can be important from those that are not. A half-life of 3 months to 5 years for loss processes may be a useful cutoff range for estimations: those processes with half-lives over 5 years can be confidently excluded from further consideration, and those with half-lives of less than 3 months can be confidently carried into the next assessment level. Those processes with half-lives in the cutoff range may then be scrutinized for more accurate estimates or may be carried through to the next assessment level. If estimates made for the second level screening are comparable in magnitude, then measurements may be essential to distinguish among possible competing processes. If, however, one or two processes are estimated to be dominant and the estimation methods for these processes are accurate, precise, and reliable, then only these processes need be measured. It is unlikely that final hazard assessments or regulatory action can be taken based on estimation methods alone. However, such estimates will greatly expedite the assessment process and be very cost effective in identifying the processes that do require measurements.

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Wiberg, K. B. 1964. Physical Organic Chemistry. John Wiley and Sons, Inc., New York.

5 MOLECULAR WEIGHT, MW

The MW is used to calculate the concentration of a chemical in molar units and to estimate gas phase diffusion coefficient volatilization rate ratios. The calculation of MW is a simple procedure familiar to almost everyone. In calculating the molecular weight for use in volatilization estimates, the possibility of dissociation, association or hydration equilibria should be considered in calculating the correct MW of the chemical species in aqueous solution.

5.1 Estimation Method

The MW is readily calculated for most chemicals from its molecular structure and atomic weight data. For oligomers or higher molecular weight polymers, the molecular weight(s) used in an assessment may have to be assumed from a range of MWs obtained by calculations based on monomer units.

5.2 Limitation of Method

Most MW values are readily obtained by calculation, although they can be measured. The calculated MW values are reliable if the chemical structure is correct and usually good to within 0.01 g-atomic weight.

5.3 Recommendation

No further work for estimating molecular weight is necessary.

6 OCTANOL/WATER PARTITION COEFFICIENT, K_{ow}

K_{ow} values are used to estimate K_{oc} and S_w values using correlation equations. K_{ow} values are not environmental parameters themselves, but they are useful to indicate the partitioning of a chemical between organic media and water. K_{ow} data, sometimes expressed in $\log_{10}$ form as log P, have been extensively used in medicinal and toxicological studies to predict partitioning of chemicals in biological systems. As a historical note, n-octanol was chosen as the organic phase for the partitioning measurement because n-octanol was considered similar to lipid and fatty-tissue substances, and it was readily available so that it could become a standard solvent for the partitioning experiment. Partition coefficients for chemicals distributed between other solvents (e.g., hexane, benzene, olive oil) and water also have been reported, but a much larger data base exists for the octanol/water system.

6.1 Estimation Method

Several fragment additivity methods are used to calculate K_{ow} values. These fragment values were developed using data from the Pomona College Medicinal Data Base. The calculation of K_{ow} values has been discussed and described by Lyman et al (1982). Several computer programs are available for performing these calculations, but all calculations still require some review and manual corrections by experts to allow for special effects (notably H-bonding and polar effects). Because the fragment additivity values are based on regression analyses using measured K_{ow} values, the accuracy of the method depends on the quality and extent of the original data base and this data base is under continuing review and expansion. Discussion of error propagation in calculation of K_{ow} values is usually limited to the average error of the differences between measured and calculated K_{ow} values. This type of error analysis is valid only for the members of the original data base; assuming a similar error would be incurred in the calculation of a new K_{ow} value is operationally useful, but it is not statistically valid for predicting the precision of a new value (see 4.4).

Although correlations exist between K_{ow} and the parameters K_{oc}, and S_w, values of K_{ow} seldom are calculated from these parameters because they are usually more difficult to obtain and are less reliable. The correlations do serve as a valuable cross-check on calculated K_{ow} values, serving to identify possibly incorrect values that require reevaluation of both values.

Lyman et al. (1982) note that correlations between K_{ow} values and partition coefficients measured in other organic solvent/water systems can be used to estimate K_{ow} values. This estimation method is only necessary in the rare occasion when K_{ow} values cannot be calculated from available fragment parameters, and a partition coefficient is available in the second organic solvent/water system.

It is also probable that K_{ow} values may be correlated with the molecular surface (ms) parameters (Yalkowsky and Valvani, 1976). Because both ms and K_{ow} can be obtained directly from SAR methods, it is unlikely that a correlation of K_{ow} with ms is useful except as a link between ms and K_{oc} or S_w.

6.2 Limitations of Method

Most K_{ow} values now used in environmental assessments are probably estimated, but the accuracy and precision of the values are generally not evaluated or cannot be evaluated from information available. However, in other correlations the estimated and measured values usually agree well enough for most applications. The method is limited, however, by the ability of the user to dissect chemical structure correctly for use of the K_{ow} SARs and in some cases by the user being able to correctly recognize the need for and use correction factors.

6.3 Recommendations

It is recommended that the accuracy of K_{ow} calculations be examined as a high priority. It would be preferable to use a rigorous statistical analysis, evaluating the standard error and confidence levels about each factor and then the error propagation in the K_{ow}

calculation. However, in the short term, it may suffice and be more practical to compare accurately measured values with those obtained using several of the available computer programs. This information could then be used to decide priorities for more measurements and/or data sets to be subjected to statistical analyses.

6.4 References

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York.

Yalkowsky and Valvani, 1976 (p. 26 in text).

7 SEDIMENT/WATER PARTITIONING COEFFICIENT, K_p

The partitioning coefficient of a chemical between sediment and water is given by

$$K_p = C_s/C_w$$

where

K_p = sediment/water partition coefficient (unitless if C_s and C_w are in same units)
C_s = amount of chemical adsorbed per unit mass of sediment
C_w = amount of chemical in solution phase at equilibrium per unit mass of solution.

Thus knowledge of K_p and the concentration of a chemical in an environmental body of water can be used to estimate the amount of chemical adsorbed on sediment; knowledge of K_p and concentration of chemical in sediment may also be used to estimate a chemical concentration in water. For sufficient dilute concentrations of chemicals the adsorption isotherm (C_s versus C_w at constant temperature) is linear and K_p is the slope of the isotherm.

7.1 Estimation Method

K_p values for a sediment can be estimated from K_{oc} values if the organic carbon fraction of the sediment, f_{oc}, is known and if it is assumed that hydrophobic interactions dominate the sorption process (see Section 8.4).

$$K_p = K_{oc}\ f_{oc}$$

It is probable that sorption of some chemicals may be dominated by ion-exchange or complexation phenomena and that the use of K_{oc} values alone will underestimate K_p values for these chemicals.

As a point of definition, the term hydrophobic has been used in this report to describe the interaction of nonpolar organic species with water because of the widespread use of this term by researchers in the field of environmental fate assessment. However, as Hildebrand (1979) has pointed out, there is no hydrophobia between water and nonpolar organics such as alkanes; there is only a lack of hydrophilia to break the hydrogen bonds of water to allow dissolution of hydrocarbons. Although some researchers have argued that the negative entropy of solution of alkanes in water suggests that a rigid water structure is formed around nonpolar solutes, there is no direct evidence for these structures and the loss of entropy can be explained by simpler theories.

Hildebrand and Miller (1968) showed that the loss of entropy caused by dissolving alkane gases in water varied linearly with the two-thirds power of the molal volume of the gases at their boiling point and thus is a function of alkane molecular surface area. This is consistent with the Pople model of water molecules all bonded together by the maxiumum number of flexible hydrogen bonds. It is also of interest to note that Yalkowsky (1976) has successfully correlated aqueous solubilities with calculated molecular surface areas for a wide variety of polar and nonpolar organic chemicals.

In summary, hydrophobic is a convenient and descriptive term, but unfortunately does not describe water-hydrocarbon interactions and therefore its use in this context should not be encouraged.

7.2 Limitations of Method

K_p values may be estimated from K_{oc} values if it is assumed that nonspecific (hydrophobic) phenomena dominate the sorption process. If a chemical is very polar or ionic, specific interactions may contribute to sorption; this will be especially true for cationic chemicals. For such chemicals, the organic carbon fraction of sediment, f_{oc}, may also be important in determining sorption because phenolic/carboxylic acid functions are present in humic substances, and the presence of these groups will contribute to the total ion-exchange capacity of the sediment. At low f_{oc} values, however, the inorganic fraction of sediment will probably dominate ion-exchange sorption. At present no literature data are available for comparing the relative importance of hydrophobic sorption with other sorption phenomena for organic chemicals.

7.3 Recommendations

It would appear to be of high priority to determine how and when other sorption processes other than hydrophobic phenomena may contribute to K_p values so as to accurately represent partitioning in the environment.

7.4 References

Hildenbrand, J. H. 1974. Proc. Natl. Acad. Sci. USA 76:194.

Miller, K. and J. H. Hildenbrand. 1968. J. Am. Chem. Soc. 90:301.

Yalkowsky, S. H. 1976. J. Phys. Chem. 80:829.

8 ORGANIC-CARBON NORMALIZED SEDIMENT/WATER PARTITION COEFFICIENT, K_{oc}

K_{oc} values are used to estimate K_p values for sediments of known or assumed organic carbon fraction, f_{oc}.

$$K_p = K_{oc} f_{oc}$$

The K_{oc} values are useful because they are normalized for the amount of organic carbon on the sediment used to measure K_p. Some researchers have normalized K_p values based on total organic matter to obtain K_{om} values, but K_{oc} appears to be more commonly used.

8.1 Estimation Method

By assuming that partitioning between water and the organic content of the sediment is similar to partitioning between octanol and water, researchers have attempted to correlate K_{oc} with octanol/water partition coefficients, K_{ow} (Briggs, 1973; Karickhoff et al., 1979). The success of these correlations for the physical adsorption of neutral organic species indicates the following:

(1) The average van der Waals attractive force experienced by a neutral organic species within the organic part of the sediment is well approximated by the average force exerted on the same species in bulk n-octanol.

(2) The adsorption capacity per unit mass of the organic content of sediments does not vary significantly from sediment to sediment.

Currently, at least nine different equations correlate K_{oc} values with K_{ow} or S_w values; these are listed in Lyman et al. (1982). Two of the K_{oc}-K_{ow} correlations that are frequently cited in the literature are those of Kenaga and Goring (1978) and Karickhoff et al. (1979). Their equations are significantly different and probably reflect the different data bases used to correlate K_{oc} with K_{ow}. The chemicals studied by

Karickhoff et al. were relatively nonpolar and thus satisfied assumption (1) above more closely than those chemicals correlated by Kenaga and Goring (1978). Whereas the equation of Karickhoff et al. (1979) conforms to a simple model and accurately predicts sorption coefficients from K_{ow} data for a limited class of organic chemicals, it has not been widely tested and may be highly inaccurate for a more universal set of pollutants and sediments. As the data base of reliable K_{oc} and K_{ow} grows, it may become apparent that several correlation equations may be useful to adequately predict K_{oc} values from K_{ow} values for a variety of chemical systems of interest.

No procedures are available for calculating K_{oc} values from molecular structure parameters. The success of the correlation equation between K_{oc} and K_{ow} values, with K_{ow} being calculated from the fragment additivity approach, indicates that, in principle, K_{oc} values could be calculated using an additivity approach. The lack of a large data base of reliable measured K_{oc} values makes such an effort inadvisable at this time; additionally, the error in experimental measurement of K_p values is often large, and incomplete understanding of the phenomena of sorption probably would make the direct calculation of K_{oc} no better than the correlation between K_{oc} and K_{ow} (i.e., major source of error is in K_{oc} value). The recommended correlation equation for K_{ow}-K_{oc} is that of Karickhoff et al.

$$\log K_{oc} = 1.0 \log K_{ow} - 0.21$$

8.2 Limitations of Method

Other than calculation of K_{oc} from measured values of K_p and f_{oc}, the correlation of K_{oc} with K_{ow} is the only estimation method available. From the information available, it appears that K_{oc} data used in some correlations may be suspect because it was incorrectly assumed that the K_p values measured were entirely due to hydrophobic* interactions, and therefore normalization of K_p against f_{oc} provided inaccurate K_{oc} values. If such is the case, the correlations between K_{ow} and K_{oc} are roughly correct in an operational sense for the set of chemicals studied, but are not correctly defined in a process-specific manner for all chemicals. More work on this subject should be performed if a larger and reliable set of K_{ow} and K_{oc} data become available.

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*See Section 7.1.

8.3. Recommendations

The plethora of correlations needs theoretical and statistical evaluations to determine which equations are unique and/or preferred for fate assessments. More data are also required to test for merit of the use of correlations for specific classes of chemicals as compared to more general correlations.

8.4 References

Briggs, G. G. 1973. A Simple Relationship Between Soil Adsorption of Organic Chemicals and Their Octanol/Water Partition Coefficients.

Karickhoff, S. W., D. S. Brown, and J. A. Scott. 1979. Sorption Hydrophobic Pollutant on Natural Sediment. Water Research 13, 241.

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York.

Kenaga, E. E., and C.A.I. Goring. 1978. Relationship Between Water Solubility, Soil Sorption, Octanol-Water Partitioning and Bioconcentration of Chemicals in Biota. Preprint, Amer. Soc. Testing Materials, Third Aquatic Toxicology Symposium, New Orleans, LA, October 17-18.

9 MELTING POINT, MP

Melting point data are not used directly in aquatic fate assessments except to show what phase a chemical is in if the concentration is above the water solubility. The melting point is used to estimate the decrease in solubility of a solid with reference to liquid solute reference state in calculations of S_w from K_{ow} if the melting point is greater than 25°C.

9.1 Estimation Method

Yalkowsky (University of Arizona) has recently informed SRI that he has developed a method for estimating melting points that is quite accurate and that also takes into account the problems encountered with geometric isomers.

9.2 Limitations of Method

Methods of estimating MPs and their limitations will be sought if sufficient interest is shown. It does not appear that an accurate estimation of MP is necessary for calculating S_w.

9.3 Recommendations

Because melting point data are easily measured and usually provided for solid chemicals, efforts to estimate MP data are not recommended at this time.

10. WATER SOLUBILITY, S_w

The major use of S_w values is for estimates of H_c values for calculation of volatilization rate constants. S_w values are also of interest for situations where the amount of chemical may exceed the solubility limit of a system (spill event, very low water solubility of a chemical).

10.1 Estimation Method

S_w values may be estimated from K_{ow} values or from molecular surface values, and these methods have been discussed by Lyman et al. (1982). We have recently conducted a critical evaluation of the calculation of S_w values from K_{ow} (Mabey et al., 1982). Although S_w may also be calculated from correlation equations using K_b or K_{oc} values, the latter are usually less reliable and therefore they are not practical for S_w estimations. Lyman et al. (1982) describe a method by which S_w values can be calculated from structural parameters, but this method seems tedious and of limited applicability. The correlation of K_{ow} with S_w appears to be more useful if reliable K_{ow} values are available. The recommended equation for calculation of S_w from K_{ow} is that of Yalkowsky and Valvani (1980):

$$\log S_w = -1.08 \log K_{ow} + 3.70 + \log (MW) - \left[\frac{13.6 + 2.5(n - 5)}{1360}\right](MP - 25)$$

where S_w is in ppm, n = number of flexible atoms (that are not part of multiple bonds or ring structures); if MP < 25°C, then (MP - 25) is set equal to zero.

10.2 Limitations of Method

The equation of Yalkowsky and Valvani represents the best equation for estimating S_w values if K_{ow} values are available. The limitations of this and other S_w estimation methods mainly related to the quality of S_w data in the literature, which in many cases show large discrepancies between measurements by several techniques and/or laboratories. However, recent developments in S_w measurement techniques have improved the quality of solubility data, and remeasurement of some values for improving or testing estimation methods now may be conducted. Also, the data base of Yalkowsky* would also be valuable for determining the limitations of current estimation methods.

10.3 Recommendations

Testing of existing methods, especially that of Yalkowsky and Valvani, is recommended. If a large and accurate data base is available, we also recommend that estimation methods be developed for specific classes of chemicals and that the accuracy and precision of the specific methods be tested and compared with those of the more general (e.g., class nonspecific) methods.

10.4 References

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York.

Mabey, W. R., J. H. Smith, R. T. Podoll, H. L. Johnson, T. Mill, T.-W. Chou, J. Gates, I. Waight Partridge, and D. Vandenberg. 1982. Aquatic Fate Process Data for Organic Priority Pollutants. Final Draft Report, EPA Contract No. 68-01-3867.

Yalkowsky, S. H., and S. C. Valvani. 1980. Solubility and Partitioning. I: Solubility of Non-electrolytes in Water. J. Pharm. Sci. 69:912.

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*Private communication, from S. Yalkowsky, University of Arizona.

11 BOILING POINT, BP

The major use of BP data is in the calculation of P_v, and ultimately H_c, values (see Sections 12 and 13). Currently, BP data are not directly used in fate assessments except to qualitatively indicate how rapidly the chemical may volatilize in a spill situation, and to determine whether the chemical is a gas or liquid at ambient temperatures.

11.1 Estimation Methods

Methods for estimating BP for chemicals are extensively discussed and described by Lyman et al. (1982).

11.2 Limitations of Method

In their review of the BP estimation methods, Lyman et al. (1982) discuss some limitations of each method. The limitations mainly arise from two sources: (1) the range of structures in the data base used to establish the method and (2) the ability to understand how the structure is analyzed for correct application of the method. As demonstrated by Lyman et al., the accuracy of the methods is quite good for many classes of chemicals.

11.3 Recommendations

BP data are ultimately used in estimates of volatilization rate constants via P_v and H_c calculations. Thus, it must be determined whether the accuracy of the BP estimation methods is either critical or of no consequence to their use in fate assessments (e.g., are other factors or assumptions more critical than BP data in the estimation of volatilization rates.) This question seems most relevant to EPA-OTS and the PMN efforts, because BP data are usually known or provided for other chemicals of interest to other EPA programs. A recent paper by Mackay et al. (1982) on the calculation of P_v from BP data should make estimation of BP more important for environmental assessments; therefore one or several of the available methods should be expanded.

11.4 References

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York.

Mackay, D., A. Bobra, D. W. Chan, and W. Y. Shiu. 1982. Vapor Pressure Correlations for Low-Volatility Environmental Chemicals. Environ. Sci. Technol. 16(10):645-649.

12 HEAT OF VAPORIZATION, H_{vap}

The heat of vaporization is used to calculate the vapor pressure of a chemical at a selected temperature using the Clausius-Clapeyron equation.

12.1 Estimation Methods

The heat of vaporization may be estimated using Trouton's Rule, which states that

$$\Delta H_{vap} \text{ (cal mol}^{-1} \approx 21 \text{ (BP)}$$

where BP is in Kelvins. This relationship holds well for various nonpolar organic chemicals, especially those that are not subject to hydrogen bonding. Lyman et al. (1982) discuss several methods by which heats of vaporization may be estimated from structural information. Mackay et al. (1982) have recently evaluated methods for estimating P_v from BP data for hydrocarbons and halogenated hydrocarbons (see Section 13), and specifically examined the common assumption that ΔH_{vap} does not vary with temperature. The conclusion was that assuming ΔH_{vap} is temperature independent gives P_v values that are two to three times higher than measured P_v values. Allowing for a temperature dependent ΔH_{vap}, estimated P_v values agreed with measured values within a factor of 1.25 (mean error). Because the method of Mackay et al. (1982) for estimating P_v from BP data includes estimation of the temperature dependent ΔH_{vap} term, estimation of ΔH_{vap} itself now seems unnecessary, if BP data are available.

12.2 Limitations of Methods

The comments in the section on BP estimation apply to methods for estimating the heat of vaporization.

12.3 Recommendations

No further development of methods for estimating ΔH_{vap} is recommended. If correlations of BP with P_v are successfully developed for certain classes of chemicals, as demonstrated by Mackay et al. (1982), SARs for classifying chemicals according to the temperature dependence of ΔH_{vap} may be important for selection of best correlation methods.

12.4 References

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York.

Mackay, D., A. Bobra, D. W. Chan, and W. Y. Shiu. 1982. Vapor Pressure Correlations for Low-Volatility Environmental Chemicals. Environ. Sci. Technol. 16(10):645-649.

13 VAPOR PRESSURE, P_v

Vapor pressure data are used to calculate H_c values for chemicals. P_v data also can be used to qualitatively determine how rapidly a chemical may evaporate in a spill situation. The rate of volatilization of a chemical from a water body or soil will depend on P_v and on S_w (via H_c) as well as on environmental parameters (see Section 17).

13.1 Estimation Methods

Lyman et al. (1982) have described two methods by which P_v data can be estimated from the structure of a molecule. Mackay et al. (1982) recently reported a thorough study of equations used to estimate P_v values at 25°C from BP data for hydrocarbons and halogenated hydrocarbons. The best agreement between the measured and calculated P_v values was obtained with the following equation:

$$\ell n P_v = -(4.4 + \ell n\ T_B)[1.803(\frac{T_B}{T} - 1)] - 0.803\ \ell n(\frac{T_B}{T}) - 6.8(\frac{T_M}{T} - 1)$$

where P_v is in torrs and T_B and T are the boiling point and an environmental temperature (°Kelvin), respectively, and T_M is the melting point. The calculated values of P_v for 72 chemicals were accurate to within a factor of 1.25 (mean error), and Mackay noted that this equation was not applicable to chemicals other than those in the class of hydrocarbons studied. The success of Mackay's approach suggests that further work in developing BP - P_v correlations for other classes of chemicals should be seriously considered.

13.2 Limitations of Methods

Mackay et al. (1982) have specified that their equation for estimating P_v from BP data is applicable only to hydrocarbons and halogenated hydrocarbons; however, application of their equation to some chemicals of other classes does show good agreement with measured values.

chemicals of other classes does show good agreement with measured values.

Of the two methods for estimating P_v that are described by Lyman et al. (1982), the modified Watson correlation appears to be most accurate, but is useful only for a limited but a basic set of structures. The average and maximum errors listed by Lyman et al. (1982) for estimated P_v values using the modified Watson correlation shows that the errors are greater for the lower vapor pressure values, with the average error being 40-50% for $P_v < 10$ mm.

13.2 Recommendation

A critical review of P_v data is required to determine whether the modified Watson correlation can be expanded to other classes of chemicals, or whether correlations with BP are preferred for interim use. Indeed, correlation of BP data (which are usually more reliable than P_v data) with P_v may identify suspect P_v data, which can be verified or corrected by direct measurement. Although the MacKay correlation appears to be more accurate than the modified-Watson method, the former correlation does require expertise to know when it does or doesn't apply.

13.3 References

Lyman, W. J., W. F. Reehl, and D. H. Rosenblatt. 1982. Handbook of Chemical Property Estimation Methods. McGraw-Hill, New York.

Mackay, D., A. Bobra, D. W. Chan, and W. Y. Shiu. 1982. Vapor Pressure Correlations for Low-Volatility Environmental Chemicals. Environ. Sci. Technol. 16(10):645-649.

14 HENRY'S CONSTANT, H_c

H_c values are used in calculations of the volatilization rate constant k_{vc}. If H_c is less than 10 torr M^{-1}, then a precise value of H_c may not be necessary for use in an environmental assessment because gas phase mass transfer resistance will determine the volatilization.

14.1 Estimation Method

The values of H_c can be calculated from S_w and P_v if it is assumed that liquid phase activity coefficients are constant up to the solubility limit. Mackay and Shiu (1981) have shown that measured and calculated H_c values agree within 7% for several aromatic chemicals, and therefore the assumption of constant activity coefficients is a useful one for most assessment purposes. H_c can be calculated from K_{ow} and BP data using the following equation, which is derived from the P_v/S_w relationship

$$\ln H_c \text{ (at 25°C)} = \ln K_{ow} - 0.0356(\text{BP}) - 1.504$$

This equation assumes a temperature-independent ΔH_{vap} value, which has been shown to be a source of some error in the estimate of P_v (see Sections 12 and 13). If a more accurate value of H_c is required, the equations for S_w and P_v in Sections 10 and 13 can be used to derive a more accurate expression for H_c.

Hine and Mookerjee (1975) have described a fragment additivity method for estimating H_c values. This method, along with the recent review of H_c data by Mackay and Shiu (1981), needs to be carefully evaluated to determine the limitations of the estimation method and how it may be improved to meet the data needs of EPA.

14.2 Limitations of Method

The use of H_c values estimated from the relationship P_v/S_w for volatilization estimates should be limited to chemicals with low water solubility. This is because the activity of a highly water-soluble chemicals (> 10 ppm) will vary with the concentration of the chemical. For low- solubility chemicals, however, the activity is essentially constant. Because high-water-solubility chemicals are seldom volatile, this limitation of the estimation method is usually not important in environmental assessments.

14.3 Recommendations

Since H_c is an important parameter in estimating volatilization rate constants for environmental assessments, development of methods for estimating H_c should have a high priority. However, before such a task is undertaken, S_w and P_v data should be critically reviewed because these parameters are important in the calculation of H_c.

14.4 References

Hine, J., and P. Mookerjee. 1975. The Intrinsic Hydrophilic Character of Organic Compounds. Correlations in Terms of Structural Contributions. J. Org. Chem. 40:292-298.

Mackay, D., and W. Y. Shiu. 1981. A Critical Review of Henry's Law Constants for Chemicals of Environmental Interest. J. Phys. Chem. Ref. Data 19(4):1175-1199.

15 DIFFUSION COEFFICIENT IN THE LIQUID PHASE, D_ℓ DIFFUSION COEFFICIENT IN GAS PHASE, D_g

D_ℓ and D_g are used to estimate the rate constant, k_{vc}, for volatilization of a chemical from an aquatic system. The relationships and use of D_ℓ and D_g values in evaluating volatilization rates are discussed below.

The volatilization of organic chemicals from water may depend on mass transfer in the water, in the air, or in both, depending on the magnitude of Henry's constant, H_c (Smith et al., 1980). For high volatility chemicals ($H_c > 3500$ torr L mol^{-1}), volatilization is controlled by mass transfer in the water, and it is convenient to normalize the liquid phase mass transfer coefficient of chemical (k_ℓ in cm h^{-1}) against the reoxygenation rate constant k_o of the water. Assuming that the ratio k_ℓ/k_o is constant over a range of water turbulence and also assuming that

$$(k_\ell/k_o)_{env} = (k_\ell/k_o)_{lab} \tag{15.1}$$

then the volatilization rate of the chemical in the environment (env) can be calculated if $(k_o)_{env}$ and $(k_\ell/k_o)_{lab}$ are known. Similarly, for low volatility chemicals ($H < 10$ torr L mol^{-1}) it is convenient to normalize the gas phase mass transfer coefficient of chemical k_g (cm-h^{-1}) against the water evaporation rate constant k_w of the water. The gas phase analog to equation (15.1) is

$$(k_g/k_w)_{env} = (k_g/k_w)_{lab} \tag{15.2}$$

The critical parameters for estimating volatilization rate constants then are $(k_\ell/k_o)_{lab}$ and $(k_g/k_w)_{lab}$. To estimate these ratios or to check the reliability of experimental data, it is useful to assume that

$$k_\ell/k_o = (D_\ell/D_o)^m \qquad (15.3)$$

$$k_g/k_w = (D_g/D_w)^n \qquad (15.4)$$

where D_ℓ and D_o are the diffusion coefficients of the chemical and oxygen, respectively, in water; D_g and D_w are the diffusion coefficients of the chemical and water, respectively, in air; and m and n are unitless numbers between 0.5 and 1.0 that depend on the turbulence of the liquid and gas phases respectively. For highly agitated systems m, n = 0.5 and for stagnant systems m, n = 1.0. For intermediate ranges of turbulence both m and n should have reasonably constant values between 0.5 and 1.0. Equations (15.3) and (15.4) thus imply that if the turbulence of a body of water and/or of the atmosphere can be characterized by the empirical values of m and n, then equations (3) and (4) may be used to predict volatilization rates of dissolved chemicals if their molecular diffusion coefficients are available.

15.1 Estimation Methods

Several ways of estimating diffusion coefficients have been suggested. Some investigators have suggested that the ratio of diffusion coefficients of two species in water is inversely proportional to their molecular diameters. Other investigators have followed Liss and Slater's (1974) suggestions and estimated diffusion coefficients from the relation

$$(D_1 / D_2) = (MW_2/MW_1)^{1/2} \qquad (15.6)$$

where MW_1 and MW_2 are the molecular weights of species 1 and 2 and D_1 and D_2 are the corresponding diffusion coefficients in either the liquid or gas phase.

Reid and Sherwood (1966) have discussed the limitations of these two approaches. Diffusion coefficients in solution are inversely proportional to molecular diameter only for large, spherical molecules. Gas molecules and most lower-molecular-weight organics are too small for this approximation to be good. Graham's law, on which equation (15.6) is based, is valid only for molecules effusing in a vacuum where there is no resistance to diffusion.

A more satisfying approach for predicting diffusion coefficients in water is the Othmer-Thakar relation (see Hayduk and Laudie, 1974):

$$D_\ell = 14.0/(\mu_w)^{1.1}\, V_b^{0.6} \quad (\text{in } 10^{-5}\ \text{cm}^2\ \text{s}^{-1}) \tag{15.7}$$

where μ_w is the viscosity of water and V_b is the molar volume. At 25°C the viscosity of water is 0.8904 centipoise; thus equation (15.6) simplifies to

$$D_\ell = 15.9(V_b)^{-0.6} \quad (\text{in units of } 10^{-5}\ \text{cm}^2\ \text{s}^{-1}) \tag{15.8}$$

where V_b is the molar volume at the normal boiling point. If V_b is not known, it may be estimated by the method of Le Bas (see Reid et al., 1977, p.58).

The aqueous diffusivities of 68 compounds at 25°C were calculated from equation (15.8) using V_b values calculated using the method of Le Bas. The calculated values of D_ℓ are listed in Table 15.1 together with the percent deviation of the calculated values from the experimental values (from Hayduk and Laudie, 1974). The calculated values average 2% lower than the experimental values, and the average magnitude of the deviation is 5.9%. These aqueous diffusivities were also calculated using the molecular weight relationship [Equation (15.6)]

$$D_\ell = D_\ell(O_2)\ [32/MW]^{1/2} \tag{15.9}$$

where $D_\ell(O_2)$ is the experimental diffusivity of oxygen and MW is the molecular weight of the chemical. These values, listed in Table 15.1, averaged 38% lower than the experimental values. The deviation of the calculated values from the experimental values is plotted as a function of MW in Figure 15.1. It is clear from this figure that the Othmar-Thakar equation is much more accurate (by approximately seven times) than equation (15.9) for predicting aqueous diffusivities over a broad range of molecular weights. Although the average deviation for values can be reduced by choosing a reference substance other than oxygen, it is most practical to use oxygen as a reference substance because of the relative ease of measuring reoxygenation rate constants in the laboratory and in the aquatic environment (see Smith et al., 1980).

Because the Le Bas method is very simple to use, it is clear that equation (15.7) or (15.8) is preferred over equation (15.9) if an accurate prediction of aqueous diffusivity is required; the extreme simplicity of equation (15.9) cannot be denied, however, and values calculated from it may be sufficiently accurate enough for many assessments. The Le Bas calculation can be easily done by either manual means or by an appropriate computer program.

A liquid phase mass transport coefficient for volatilization of a chemical in an aquatic environment can be estimated by combining equations (15.1), (15.3), and (15.7) to give equation (15.10):

$$(k_\ell)_{env} = (25.6/V_b)^{0.6m} [k_o]_{env} \tag{15.10}$$

where 25.6 is the molar volume (in cm^3 $mole^{-1}$) of oxygen at its normal boiling point calculated using the Le Bas method. Thus if m and $(k_o)_{env}$ are known (or can be specified) for a particular aquatic system, $(k_\ell)_{env}$ may be calculated. It may be expected that $m \sim 1$ for a lake or pond with a low level of turbulence. Smith et al. (1980) suggest that $m = 0.60$ may be appropriate for a river. Table 15.2 lists data for the volatilization of five chemicals in the laboratory under high turbulence conditions representative of rivers. The predicted ratio of D_ℓ/D_o given in Table 15.2 was calculated from

Table 15.1

CALCULATED AND EXPERIMENTAL AQUEOUS DIFFUSIVITIES AT 25°C

Substance	MW	V_b (Le Bas)[e]	D_ℓ(exp)[a]	D_ℓ($M^{-1/2}$)[b]	D_ℓ($V^{-0.6}$)[c]
NO	30	23.6	2.34	2.37 (-1.1)[e]	2.39 (-2.1)
N_2O	44	36.4	2.10	1.95 (7.0)	1.84 (12)
N_2	28	31.2	1.99	2.45 (-23)	2.02 (-1.5)
NH_3	17	25.8	2.28	3.14 (-38)	2.26 (0.9)
O_2	32	25.6	2.29	2.29 (0)	2.27 (0.9)
CO	28	30.7	2.30	2.45 (-6.4)	2.04 (11)
CO_2	44	34.0	1.92	1.95 (1.7)	1.92 (0)
SO_2	64	44.8	1.59	1.62 (-1.8)	1.62 (-1.9)
H_2S	34.1	32.9	2.10	2.22 (-5.6)	1.95 (7.1)
Cl_2	70.9	48.4	1.48	1.54 (-4.0)	1.55 (-4.7)
CH_4	16	29.6	1.67	3.24 (-94)	2.08 (-25)
CH_3Cl	50.5	47.5	1.49	1.82 (-22)	1.57 (-5.4)
C_2H_3Cl	62.5	62.3	1.34	1.64 (-22)	1.33 (0.7)
C_2H_6	30	51.8	1.34	1.64 (-22)	1.49 (-8.0)
C_2H_4	28	44.4	1.55	2.45 (-58)	1.63 (-5.2)
C_3H_8	44	74.0	1.16	1.95 (-68)	1.20 (-3.4)
C_4H_{10}	58	96.2	0.97	1.70 (-75)	1.03 (-6.2)
Pentane	72.15	118	0.97	1.70 (-75)	0.91 (6.2)
Benzene	78.12	96.0	1.09	1.47 (-34)	1.03 (5.5)
Toluene	92.15	118	0.95	1.35 (-42)	0.91 (4.2)
Ethylbenzene	106.17	140	0.90	1.26 (-40)	0.82 (8.9)
Methanol	32.04	37.0	1.66	2.29 (-38)	1.82 (-9.6)

Table 15.1 (Continued)

Substance	MW	V_b(Le Bas)^e	D_ℓ(exp)^a	$D_\ell(M^{-1/2})^b$ D_ℓ	$D_\ell(V^{-0.6})^c$
Ethanol	46.07	59.2	1.24	1.91 (-54)	1.37 (-10)
Propanol	60.11	81.4	1.12	1.67 (-49)	1.14 (-1.7)
Butanol	74.12	104	0.98	1.50 (-54)	0.98 (0)
Benzyl alcohol	108.15	126	0.93	1.25 (-34)	0.87 (6.50
Ethylene glycol	62.07	66.6	1.16	1.64 (-42)	1.28 (-10.3)
Triehtylene-glycol	150.18	170	0.76	1.06 (-39)	0.73 (3.9)
Propylene glycol	76.11	88.8	1.00	1.48 (-48)	1.08 (-8.0)
Glycerol	92.11	96.2	0.93	1.35 (-45)	1.03 (-11)
Acetone	58.08	74.0	1.28	1.70 (-33)	1.20 (6.3)
Ethylacetate	88.12	111	1.12	1.40 9-23)	0.94 (16)
Furtural	96.09	95.7	1.12	1.32 (-18)	1.03 (8.0)
Urea	60.16	58	1.38	1.67 (-21)	1.39 (-0.7)
Formamide	45.04	43.8	1.67	1.93 (-16)	1.65 (1.2)
Acetamide	59-07	66.0	1.32	1.69 (-28)	1.29 (2.3)
Propionamide	73.10	88.2	1.20	1.52 (-26)	1.08 (10)
Butyramide	87.12	110	1.07	1.39 (-30)	0.95 (11)
Diethylamine	73.14	112	1.11	1.51 (-36)	0.94 (15)
Aniline	93.13	110	1.05	1.34 (-28)	0.95 (9.5)
Formic acid	46.03	41.6	1.52	1.91 (-26)	1.70 (-12)
Acetic acid	60.05	63.8	1.19	1.67 (-40)	1.31 (-12)
Propanoic acid	74.08	86.0	1.01	1.51 (-49)	1.10 (-9)
Butyric acid	88.12	108	0.92	1.38 (-50)	0.96 (-4.3)

Table 15.1 (Continued)

Substance	MW	V_b (Le Bas)^e	D_ℓ (exp)^a	D_ℓ ($M^{-1/2}$)^b	D_ℓ ($V^{-0.6}$)^c
Valeric acid	102.13	130	0.82	1.28 (-56)	0.86 (-4.9)
Caproic acid	116.16	153	0.78	1.20 (54)	0.78 (0)
Succinic acid	118.1	120	0.86	1.19 (-39)	0.90 (4.7)
Glutaric acid	132.13	142	0.79	1.13 (-43)	0.81 (-2.5)
Adipic acid	146.12	165	0.74	1.07 (-45)	0.74 (0)
Heptanedioic acid	160.17	187	0.71	1.02 (-44)	0.69 (2.8)
Glycine	75.07	78	1.06	1.50 (-41)	1.16 (-9.4)
Alanine	89.10	100	0.91	1.37 (-51)	1.00 (-9.9)
Serine	105	108	0.88	1.26 (-44)	0.96 (-9.1)
Aminobutyric acid	103.12	122	0.83	1.28 (-54)	0.89 (7.2)
Valine	117.15	145	0.77	1.20 (-55)	0.80 (-3.9)
Leucine	131.18	167	0.73	1.13 (-55)	0.74 (-1.4)
Proline	115.13	127	0.88	1.21 (-37)	0.87 (1.1)
Histidine	155.16	168	0.73	1.04 (-42)	0.73 (0)
Phenylalanine	165.19	189	0.705	1.01 (-43)	0.68 (2.8)
Tryptophan	204.23	223	0.66	0.91 (-37)	0.62 (6.1)
Triglycine	189.17	198	0.665	0.94 (-42)	0.66 (0.1)
Glycyl-leucine	188.23	227	0.623	0.94 (-52)	0.613 (1.6)
Leucyl-glycine	188.23	227	0.613	0.94 (-54)	0.613 (0)
Amino benzoic acid	137.14	144	0.84	1.11 (-32)	0.81 (3.6)
Dextrose	180.16	166	0.675	0.97 (-43)	0.74 (-9.6)
Sucrose	342.3	325	0.523	0.70 (-34)	0.495 (5.5)

Table 15.1 (Concluded)

Raffinos	594.5	480	0434	0.53 (-22)	0.391 (9.9)
	Average	(-38%)			(-2.0%)
Absolute average deviation		38%			(5.9%)

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[a] All diffusivities are in cm^2 s^{-1} x 10^5.
[b] $D_1(M^{-1/2})$ = $D(O_2)$ $(32/M)^{1/2}$ where $D(O_2)$ is the experimental diffusivity of oxygen in water.
[c] The molar volume of the normal boiling point, V_b, was calculated by the method of Le Bas.
[d] $D(V^{-0.6})$ = 15.9 $(V)^{-0.6}$ from the Othmer-Thakar equation.
[e] Numbers in parentheses are percent deviations of calculated from experimental values.

Table 15.2

COMPARISON OF PREDICTED AND MEASURED VALUES OF k_ℓ / k_o

Compound	D_ℓ/D_o [a]	Predicted	Measured	k_ℓ/k_o $(32/M)^{1/2}$
Benzene	0.45 (0.48)	0.62	0.56 ± 0.03[b]	0.64
Carbon dioxide	0.84 (0.90)	0.90	0.89 ± 0.03[c]	0.85
Ethylene	0.70 (0.68)	0.81	0.87 ± 0.02[d]	1.06
Propane	0.53 (0.51)	0.68	0.72 ± 0.01[d]	0.85
Krypton	0.83 (0.84)	0.89	0.82 ± 0.08[c]	0.62

measure predict

---

[a] Numbers in parentheses are experimental values of D_ℓ/D_o.
[b] Smith, et al. (1980).
[c] McCarthy et al. (1973).
[d] Rathbun et al. (1978).

$$D_\ell/D_o = (25.6/V_o)^{0.6} \tag{15.11}$$

and the predicted value of k_v/k_o given in Table 15.2 was calculated from

$$k_v/k_o = (D_\ell/D_o)^{0.6} = (25.6/V_b)^{0.36} \tag{15.12}$$

The predicted values ofD_ℓ/D_o and k_v/k_o are in excellent agreement with experimental values as shown in Table 15.2.

A useful equation for predicting vapor diffusion coefficients, D_g, in air (Wilke and Lee, 1955) is:

$$D_g = \frac{BT^{2/3}\left(\frac{1}{MA} + \frac{1}{MW}\right)^{1/2}}{\sigma_{Ac}^2 \Omega} \text{ in cm}^2\ \text{s}^{-1} \times 10^2 \tag{15.13}$$

where

B = $0.214 - 0.05\left(\frac{1}{MA} + \frac{1}{MW}\right)^{1/2}$
T = temperature, K
MA = molecular weight of air (28.964)
MW = molecular weight of chemical
σ_{AC} = collision diameter = $(\sigma_A + \sigma_c)/2$
where $\sigma_A = 3.617$ and $\sigma_c = 1.18\ V_b^{1/3}$
Ω = collision integral
T^* = $T/[97.0(1.15)BP]^{1/3}$
BP = normal boiling point

The vapor phase diffusion coefficient can thus be calculated from a knowledge of MW, V_b, and BP. Values of D_g/D_w calculated at 298°K from equation (15.13) using Le Bas values of V_b are listed in Table 15.3. The value of the collision integral Ω (based on the Lennard-Jones potential) in equation 15.13 was taken from a table of (T^*) values given by Hirshfelder et al. (1954). Table 15.3 and Figure 15.2 clearly show that the Wilke-Lee equation predicts the value of D_g/D_w much more accurately than equation (15.6).

15.2 Limitation of Method

Figures 15.1 and 15.2 demonstrate that current estimation methods based on structure accurately estimate diffusion coefficients. The figures also show that use of MW may adequately estimate diffusion coefficients for screening and other preliminary assessments.

15.3 Recommendations

Other than measurement of more diffusion coefficients to test existing methods, no further work on estimation methods seems necessary.

15.4 References

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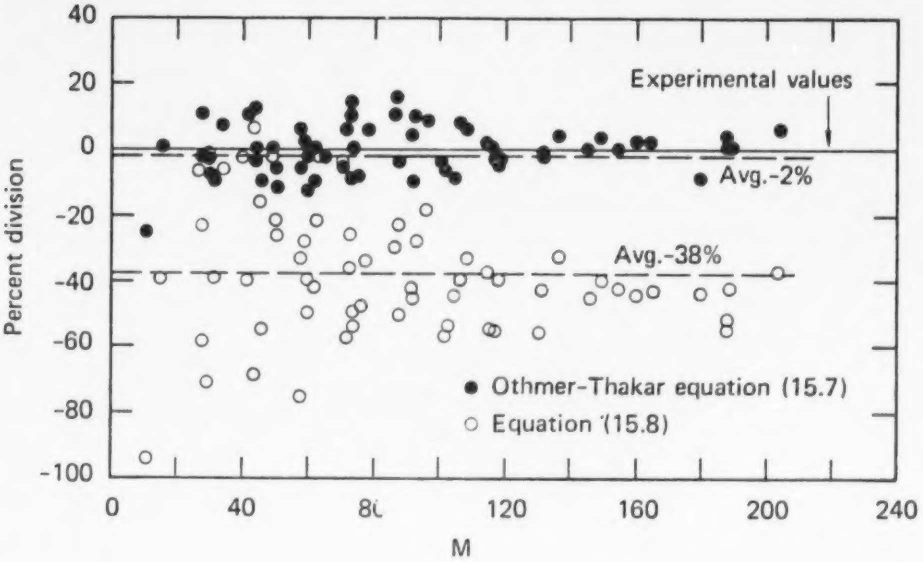

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Figure 15.1 Deviations of calculated aqueous diffusivities from experimental values as a function of molecular weight at 25°C.

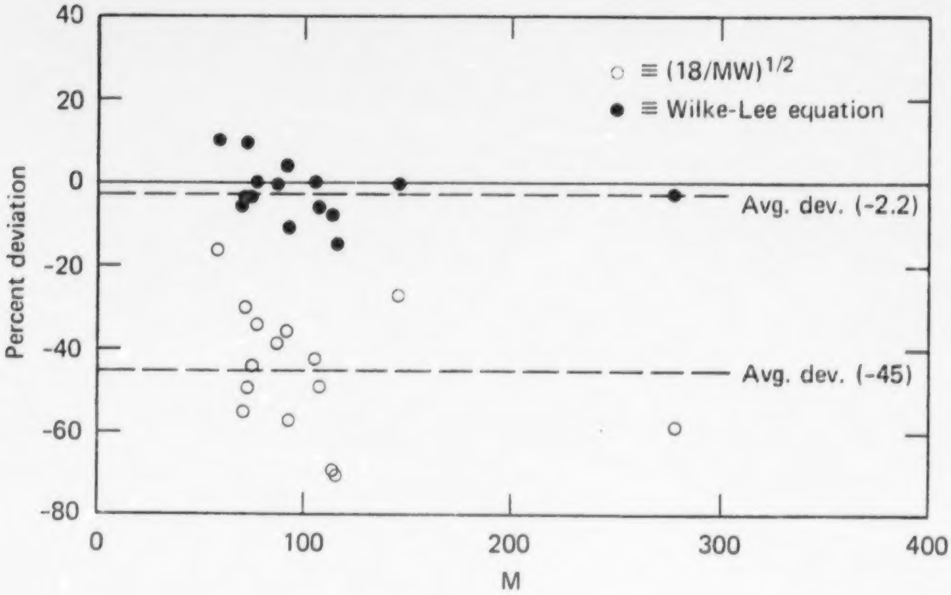

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Figure 15.2 Percent deviations of calculated values from experimental values of D_g/D_w as a function of molecular weight at 298 K.

Table 15.3

CALCULATED AND EXPERIMENTAL VALUES OF VAPOR DIFFUSIVITIES IN AIR

Compound	M	$(D_g/D_w)^a$	W-L[b]	$(18/M)^{1/2}$
Pentane	72.15	0.323	0.341 (-5.6)[c]	0.50 (-55)
Octane	114.23	0.236	0.255 (-8.1)	0.40 (-68)
Benzene	78.15	0.357	0.357 (0.0)	0.48 (-34)
Ethylbenzene	106.17	0.289	0.288 (0.4)	0.41 (-42)
1,1,2,2-Tetra-chlorethane	146.2	0.277	0.278 (-0.4)	0.35 (-27)
Dibutylphthalate	278.35	0.161	0.166 (-2.8)	0.25 (-58)
Aniline	93.13	0.281	0.313 (-11)	0.44 (-57)
Acetic acid	60.05	0.473	0.425 (10)	0.55 (-16)
Benzyl alcohol	108.15	0.274	0.291 (-6.0)	0.41 (-49)
Toluene	92.15	0.327	0.317 (3.1)	0.44 (-35)
Butanol	74.12	0.331	0.342.(3.5)	0.49 (-49)
Propylene glycol	76.11	0.338	0.350 (-3.6)	0.49 (-44)
Ethylacetate	88.12	0.331	0.333 (-0.7)	0.45 (-37)
Diethylamine	73.14	0.382	0.346 (9.5)	0.50 (-30)
Caproic acid	116.16	0.231	0.267 (-15)	0.39 (-70)
	Avg.	(-2.2)	(-45)	
	Avg. dev.	5.3%	45%	

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[a] Experimental values taken from Lugg (1968). $D_w = 0.026$ cm^2 s^{-1}.

[b] Calculated using Wilke-Lee equation (15.13) with Le Bas molar volumes V_b.
Number in parentheses are percent deviations from experimental values.

16 REAERATION RATE RATIO, k_v/k_o

The ratio of the rate constant for loss of chemical from solution to the rate constant of oxygen uptake by solution is used to calculate a volatilization rate constant of chemical $(k_v)_{env}$ in the environment,

$$(k_v)_{env} = (k_o)_{env}(k_v /k_o)_{lab} \qquad (16.1$$

where $(k_o)_{env}$ is the rate constant for reaeration of the environmental water body; this equation only holds for chemicals where liquid phase mass transport is dominant.

16.1 Estimation Method

The ratio k_{vc}/k_{vo} can be estimated from liquid phase diffusion coefficients or from molecular weight for the chemical and oxygen. The methods are discussed and evaluated in the previous section on D_ℓ and D_g estimations.

16.2 Limitation of Method

Estimation of the reaeration rate ratio is only necessary for high-volatility chemicals (Section 15). As discussed in Section 15, the ratio can be accurately calculated using an existing SAR if molar volume data are available. The ratio may also be estimated from MW with some loss of accuracy.

16.3 Recommendation

No further work on the estimation of k_{vc}/k_{vo} is necessary at this time.

17 VOLATILIZATION RATE CONSTANT, k_{vc}

The first-order rate constant for volatilization depends on both physiochemical properties and on environmental parameters and can be used directly in an assessment or fate model. The user must choose the temperature and the mass transfer coefficients for gas and liquid phases. The complete equation for calculating the volatilization rate constant for a chemical in a water body of depth L and temperature T is as follows:

$$k_v = 1/L\left[k_\ell[(D_\ell/D_o)^m]^{-1} + RT[H_c k_g(D_g/D_w)^n]^{-1}\right]^{-1} \qquad (17.1)$$

where k_ℓ and k_g are environmental parameters m and n are constants as discussed in section 15.

17.1 Estimation Method

Values of k_v can be calculated using the equation (17.1).

17.2 Limitations of Estimation Method

Values of k_v can be calculated with D_ℓ, D_g and k_v/k_o data for the chemical; the environmental parameters for depth, temperature and mass transfer coefficients must be known or chosen for this calculation. The expression represents current understanding of the volatilization process, which, however, needs testing.

17.3 Recommendation

It is recommended that results calculated using equation (17.1) be tested in the laboratory and under field conditions to determine any limitations of the estimation method.

18 IONIZATION CONSTANTS, K_A or K_B

Ionization constants are used to determine the species present in solution at a specific pH. Ionic species are usually much more soluble than the neutral species, and the reactivity of the species is also usually different. If several species are present in solution, the transformation and transport of each should be evaluated. Then, depending on the dominant removal process, one species may be considered as a source of the other (i.e., as a neutral form is volatilized or transformed, equilibrium would shift to produce neutral species from the ionic form).

18.1 Estimation Methods

There is a vast literature base of K_A and K_B data for organic and inorganic chemicals from which to judge whether neutral or ionic (or both) species of chemicals will exist in aquatic systems. Quantitative SARs for calculating the K_A and K_B values for several classes of chemicals have reviewed by Wells (1962) and discussed by Lyman et al. (1982.)

As part of a tiered SAR system, more information on the acidity or basicity of chemicals needs to be available without having to calculate a value or to search the vast compilations. Some of this information can be summarized for an SAR system from the extensive compilations of K_A and K_B data available (Kortum et al., 1961; Perrin, 1965). A qualitative SAR should list the chemical structure and the range of pK_A or pK_B values for structures having generalized substituents that cause these values to change significantly. Other effects on the pK_A or pK_B values could be summarized in concise text accompanying the data, if necessary. pK_A or pK_B would be listed as limiting values if they are less than 2 or greater than 12; for pK_A or pK_B between 2 and 12 specific values should be listed because they may be important for environmental assessments that include natural waters ranging from pH 4 to 10. The qualitative SARs should also include information on whether quantitative SARS are available for actual calculation of pK_A or pK_B values if the system user should require data. Examples of qualitative SARs for phosphonic and phosphinic acids are given in Tables 18.1 and 18.2.

18.2 Limitation of Methods

A large body of K_A and K_B data can be used to determine whether the neutral or ionic species of chemicals will occur in aquatic environments of a specified pH, and both qualitative and quantitative SARs appear to be useful for EPA purposes. Further evaluation of the limitations and testing of K_A SARs should also be conducted for particular classes of chemicals of interest to EPA.

18.3 Recommendations

Because large collections of K_A and K_B data already exist in various common handbooks and in compilations of acidity/basicity data, priorities for developing qualitative SARs and the chemicals of particular interest to EPA program offices need to be identified. The SARs for K_A summarized by Wells (1962) have been tested by Lyman et al. (1982), who found a wide range of agreement between measured and estimated values depending on the particular SAR and the test chemical used. As an example of the limitation of one SAR, the K_A value predicted for bromoacetic acid was 15% lower than the measured value, whereas the K_A value predicted for trifluoroacetic acid using the same SAR was 17 times greater than the measured value. This example demonstrates the necessity for caution in the application of SARs, although in this case because the $K_A \approx 10^{-3}$ (or $pK_A < 3$), the error is of no consequence in an environmental assessment.

18.4 References

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Table 18.1

SAR for K_A: PHOSPHONIC ACIDS[a]

Structure: $R\text{-}PO_3H_2$

R	pK_1	pK_2	Range
Alkyl	2.3-2.9	7.1-9.0	CH_3 to dodecyl (12)[b]
$(Cl_nH_{3-n}C)$	1.1-1.6	4.8-6.7	$ClCH_2$- to Cl_3C- (3) ICH_2, $BrCH_2$ (2)
$(X\text{-}CH_2^-)$	1.1	4.7	
Aryl	1.1-2.4	4.7-7.8 on aryl ring.	>20 Varied substituents

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[a] Source: Kortum et al., (1964)
[b] Number in parentheses is the number of chemicals in the data base.

Table 18.2

SAR FOR K_A: PHOSPHINIC ACIDS[a]

Structure: $R\text{-}PO_2H_2$

R	pK	Range
Alkyl	3.1-4.2	CH_3 to $(CH_3)_3C$- (6)[b]
Aryl	2.1-2.4	p-Br to p-$(CH_3)_2N$- (4)[b]

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[a] Source: Kortum et al. (1964).
[b] Number in parentheses is the number of chemicals in the data base.

19 HYDROLYSIS RATE CONSTANT, k_h

The first-order hydrolysis rate constant, k_h, at a given pH is dependent on the acid, base, and neutral rate constants, the pH of the solution/aquatic environment, and is given by the equation

$$k_h = k_A[H^+] + k_N + k_B(K_w/[H^+]) \tag{19.1}$$

where K_w is the autoprotolysis constant. If k_h is known at the temperature and pH of interest to an assessment, it obviously may be used directly in a fate assessment. Use of the rate constant at other pHs may be incorrect because the relative importance of the component processes may be different, and the error in its use will depend on the relative values of k_A, k_B, and k_N.

19.1 Estimation Method

Values of k_h may be estimated by reference to data on similar chemicals if the pH-log k_h profile of the chemical class is known (Mabey and Mill, 1978). The value of k_h at a particular pH may also be estimated from k_A, k_B, and k_N values according to equation (19.1). If all values of k_A, k_B, or k_N are not available, a lower limit on k_h can sometimes be usefully estimated with the rate constants that are available; of course, k_h will be underestimated if the missing values are important.

In addition to values of k_A, k_B, and k_N available in the literature or obtained by SAR methods (see Sections 20, 21, and 22) that can be used to calculate k_h using equation (19.1), there is considerable information on the hydrolysis rates of chemicals in limited pH ranges that may also be useful for fate assessments. Some of this information cannot be accurately expressed as the specific rate constants k_A, k_B, or k_h because several of the component hydrolysis processes may have contributed to k_h. As part of an estimation system, it is useful to provide some of this information in screening-level SARs for classes of chemicals, listing the hydrolysis half-lives at pH 7 and 25°C according to subclasses of chemicals with generalized stuctural features. Tables 19.1, 19.2 and 19.3 show screening-level SARs for several classes of chemicals. These SARs also list the pH regions in which acid- or base-promoted processes may be important for the particular structural subclass and a synopsis on the reactivity of the class. The primary purpose of such screening-level SARs for k_h is to (1) provide enough information for the system user to decide whether hydrolysis may be an important process within the time scale of a particular assessment, (2) allow the user to decide whether pH of the aquatic system may be important for hydrolysis of the particular chemical, and (3) direct the user to further sources of information or to SARs for the specific acid, base, or neutral processes. If no information on the importance of acid- or base-promoted reactions is available, appropriate notations in the screening SAR could be included (see examples in the tables).

19.2 Limitations of Method

The value of k_h at a particular pH is determined by the relative values of k_A, k_B, and k_N. Because the value of k_h can vary with pH, quantitative SARs are thus not possible for estimating k_h values directly. Qualitative SARs as described above are useful, however, for assisting system users in determining what typical hydrolysis half-lives may be at pH 7 and 25°C. These SARs would be used to determine whether hydrolysis is important within the context of a particular assessment and would allow the user to determine whether neutral, or acid- or base-promoted processes are important for the chemical of interest. We recommend that half-lives be cited for a k_h SAR to forestall confusion and misuse of a k_h values; additionally, half-lives are readily used in a screening- level assessment.

19.3 Recommendations

We recommend that qualitative SARs for k_h be developed as a high priority.

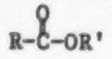
19.4 References

Kirby A. J. 1972. In: Comprehensive Chemical Kinetics, Vol. 10, C. H. Bamford and CFH Tipper, Ed. Elsevier, New York.

Mabey, W. R., and T. Mill. 1978. Critical Review of Hydrolysis of Organic Compound in Water Under Environmental Conditions. J. Phys. Chem. Ref. Data 7:383.

Table 19.1

SAR For k_h: ALIPHATIC ESTERS AT pH 7, 25°C[a,b]



$R\text{-}\overset{O}{\overset{\|}{C}}\text{-}OR'$

			pH Dependence	
R	R'	$t_{1/2}$	Acid Rxn	Base Rxn
Alkyl	1°, 2° Aliphatic alkyl	2-100 y	Up to 6	Down to 6
X-CH_2 X = halide	1°, 2° Aliphatic	Minutes to 1 mo.	Up to 3	Down to 5
Alkyl	Vinylic	10-100 d	Up to 3	Down to ~ 6
Alkyl	3° Aliphatic	140 y	Up to 7	Down to 6

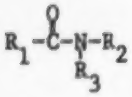
---

[a] Sources: Mabey and Mill 1978; Kirby 1972; Mill et al. (1982).

[b] Synopsis of Reactivity:
Both k_A and k_B may be important.
Electron-withdrawing groups increase k_B, have small effect on k_A.
Steric effects on hydrolysis usually minimal. k_N important for strong electron-withdrawing groups on R.

Table 19.2

SAR FOR k_h: ALIPHATIC AMIDES AT pH 7, 25°C[a,b]



$R_1-\overset{O}{\overset{\|}{C}}-\underset{R_3}{\underset{|}{N}}-R_2$

				pH Dependence	
R_1	R_2	R_3	$t_{1/2}$	Acid Rxn	Base Rxn
Alkyl	H	H	> 500 y	Up to 7	Down to 7
X_n-CH_{3-n} (X = halide)	H	H	0.23 - 1 y	Up to 5	Down to 5
Alkyl	Alkyl	H	>> 500 y	Up to 6	Down to 6
Alkyl	Alkyl	Alkyl			

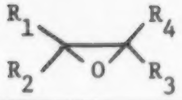
---

[a] Source: Mabey and Mill (1978).

[b] Synopsis of Reactivity: Both k_A and k_B may be important. Substituent effects similar to aliphatic esters. No data to substantiate importance of k_N in hydrolysis.

Table 19.3

SAR FOR k_H: EPOXIDES AT pH 7, 25°C[a,b]

		pH Dependence	
	$t_{1/2}$	Acid Rxn	Base Rxn
R = saturated aliphatic or H	5-28 d	3-7	Above 11
R = allylic aliphatic	4-60 m	4-8	Above 11
R = electron withdrawing substituents	Very slow	Not likely	Unknown

---

[a] Source: Mabey and Mill (1978).

[b] Synopsis of Reactivity: Base-promoted hydrolysis usually not important below pH 11. Ability of R groups to stabilize carbonium intermediate increases k_A; similar but less effects of R on k_N values.

20 ACID-PROMOTED HYDROLYSIS RATE CONSTANT, k_A

The value of k_A is used with k_B and k_N data to calculate k_h (see Section 19). A moderate amount of information and data are available on the hydrolysis of organic chemicals by acid-promoted processes, some of which has been expressed in quantitative SAR form. However, in some cases, the processes by which acid-promoted processes occur are often poorly understood therefore the SARs for k_A must be used with caution because sometimes several acid-promoted processes may be possible for one functional group on a structure.

20.1 Estimation Method

A large body of literature data is available to identify those functional groups that undergo hydrolysis (Mabey and Mill, 1978). These data are useful for determining whether acid-promoted hydrolyses may be important in aquatic systems and in some cases can be formulated as SARs or rules for evaluating k_A. For some chemicals, qualitative SARs can be developed for providing limiting rate constants (maximum or minimum values). Although some quantitative SARs are available for estimating k_A values for some chemicals, most methods are for mixed solvent systems and/or at temperatures above ambient and therefore of little use. Use of these qualitative and quantitative SARs may require some expertise or review by knowledgeable persons to select the correct SAR because several acid-promoted mechanisms are possible for some functional groups (see Hine, 1965; Gould, 1959).

As part of an SAR system, a screening SAR demonstrating the effect of pH on the hydrolysis half-life of a chemical has been suggested for the first-order hydrolysis rate constant k_h (see Section 19). If an acid-promoted hydrolysis process is judged to be important for a particular assessment on a chemical, a screening SAR for k_A can be used for showing how the value of k_A varies with molecular structure. A qualitative SAR for k_A would be a set of chemicals expanded from those listed in the k_h SAR and would list the rate constant k_A along with other information regarding the mechanism or limitations of the value. When available, the existence of a quantitative SAR for a particular functional group would be noted. The system user would then have the option of calculating a value of k_A. Examples of SARs for k_A for classes of chemicals are shown in Tables 20.1 and 20.2, which are similar in format to those for k_B (see Section 22).

For the presentation of quantitative SARs used to estimate k_A values, we recommend that the particular structure of interest be shown along with the SAR equation and that the correlation coefficient and number of data points used to establish the SAR be listed. The range of values for the substituent parameter(s) used in deriving the equation should also be listed. We suggest that actual data bases containing the rate constants and substituent constants used to determine the SAR be contained in a subfile for reference as the user may choose, but that they need not be listed with the equation and statistical information.

20.2 Limitations of Method

There is a moderate amount of data available that may be shown as qualitative SARs for k_A values, and a few quantitative SARs are also available. However, several mechanisms for the acid-promoted hydrolysis of certain functional groups have been suggested; therefore use of SARs and even estimation of k_A values by analogy to reliable k_A data must be done with caution. The knowledge that some functional groups are not sensitive to acid-promoted processes and that some k_A values are not sensitive to structural features is also available and important for inclusion in an SAR system.

20.3 Recommendation

Qualitative SARs for k_A should be developed using available data. Some of this information can be expressed as limiting rate constants based on extrapolation from higher temperature or from data obtained in mixed solvent systems; these data would suffice for assessment purposes when k_N or k_B are dominant processes.

20.4 References

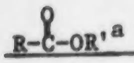
Hine, J. 1962. Physical Organic Chemistry. McGraw-Hill, New York.

Gould, E. S. 1959. Mechanism and Structure in Organic Chemistry. Hold-Rinehart and Winston. New York.

Mabey, W. R., and T. Mill. 1978. Critical Review of Hydrolysis of Organic Compound in Water Under Environmental Conditions. J. Phys. Chem. Ref. Data 7:383.

Table 20.1

SAR for k_A: ALIPHATIC ESTERS AT 25°C, VARIATION OF R, R'



$R-\overset{O}{\overset{\|}{C}}-OR'^{a}$

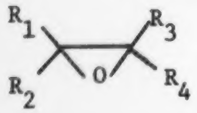
R	R'	Range of $10^4\ k_A\ (M^{-1}\ s^{-1})$	R, R'	
Alkyl 1°, 2°	Alkyl	1.3-0.6	Me to iPr	(9)
Alkyl 3°	Alkyl	1.26	t-Bu	(1)
Alkyl	Alkyl	1.1-2.33	Me to Cl_2CH	(2)

---

[a] Underlined R or R' is the varied group in the last column.
[b] Number in parentheses is the number of chemicals in the data base.

Table 20.2

SAR FOR k_A: EPOXIDES AT 25°C, VARIATION OF R_n



$R_1\ R_2\ R_3\ R_4$	Range of $10^3\ k_A\ (M^{-1}\ s^{-1})$	R	
Alkyl, H (noncyclic)	6800 - 11	Me to CH_2Br	(10)[a]
Alkenyl, H (cyclic)	$10^3 - 10^7$	Cyclo-2-hexenyl to cyclohexadienyl	(5)[a]

---

[a] Number in parentheses is number of chemicals in the data base.

21 NEUTRAL HYDROLYSIS RATE CONSTANT, k_N

The value of k_N is used with k_A and k_B data to calculate k_h (see Section 19). The term "neutral" refers to the fact that this hydrolysis process is pH independent, with the chemical reacting with water as the rate-limiting step. Because the concentration of water in a hydrolysis reaction in pure water is essentially constant [55.5 M], the second-order rate constant for reaction of chemical with water, k_{H_2O}, is combined with the water concentration term as a first-order rate constant k_N.

21.1 Estimation Method

Only limited data for a few classes of chemicals are available that can be used to develop SARs,for estimating k_N and these data must be used with caution. The lack of confidence in use of k_N data is due in part to insufficient data to determine the importance of acid- or base-promoted processes in a reported k_h (or k_N) value. In developing and applying estimation methods for k_N, it is important to recognize that very little information is available about the mechanism by which water effects transformation of chemicals in the pH-independent process because water may act as an acid or a base. Qualitative k_N SARs for alkyl chlorides and epoxides are shown in Tables 21.1 and 21.2.

In recent work at SRI, we have measured hydrolysis rate constants for several chlorinated ethanes at pHs of 5 (or 7) and 11 (Mabey and Barich, 1982; Mill et al., 1982). We found that at pH 11, the addition of chloride substituents to the ethane backbone increase k_h; products from the elimination of HCl were formed from the two tetrachloroethanes (see Section 22). At the lower pH, however, added chlorines slowed the hydrolysis rate for several chemicals, but increased the rates for others; the elimination product, trichloroethylene, was a hydrolysis product of 1,1,2,2-tetrachloroethane at pH 7 and 55°C. If we reasonably

Table 21.1

SAR FOR k_N: ALKYL HALIDES AT 25°C, VARIATION OF R, X[a]

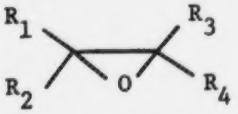
R - X			
R	X	Range of k_N (s^{-1})	R
Alkyl	F	10^{-4} - 10^{-6}	Me, t-Bu (2)[b]
1° Alkyl	Cl	2×10^{-8} - 2×10^{-7}	Me, Et (2)[b]
2° Alkyl	Cl	2.1×10^{-7}	iPr (1)[b]
3° Alkyl	Cl	3×10^{-2}	t-Bu (1)[b]
1° Alkyl	Br	$2\text{-}4 \times 10^{-7}$	Me - nPr (3)[b]
2° Alkyl	Br	4×10^{-6}	iPr (1)[b]
3° Alkyl	Br	> k_N tBuCl	--
1° Alkyl	I	7.3×10^{-8} - 1.6×10^{-7}	Me, Et (2)[b]
2° Alkyl	I	3×10^{-6}	iPr (1)[b]
3° Alkyl	I	> k_N tBuCl	--

---

[a] Reference: Mabey and Mill (1978).
[b] Number in parentheses is the number of chemicals in the data base.

Table 21.2

SAR FOR k_N: EPOXIDES AT 25°C, VARIATION OF R_N



R_1 R_2 R_3 R_4	Range of 10^7 k_N (s^{-1})	R_N
Alkyl, H (noncyclic)	2.84 - 11.1	CH_3, H, CH_2X (X = Cl, OH)
Alkenyl, H (cyclic)	Up to 10^4	Cyclo-2-hexenyl to cyclohexadienyl

---

[a] Reference: Mabey and Mill (1978).

assume that the neutral hydrolysis process was occurring by an elimination process at the lower pH values, a change in the mechanism for neutral hydrolysis can explain these observations as follows: Added chlorines generally slow the substitution of Cl for OH via a simple solvolysis process, but two chloride substituents on a carbon bearing a hydrogen increase the acidity of that hydrogen, facilitating the elimination process. Although more information is required (e.g., more accurate rate constants at lower temperatures and product analyses), this explanation is reasonable by reference to the k_B results because elimination of HCl catalyzed by water requires more activation of hydrogen (two chlorides on the same carbon), whereas the better base (OH^-) requires less activation (one chloride substituent). The rules for identifying the possibility of water-catalyzed elimination (rate constant k_{EN}) are probably similar to those for k_{EB} in Section 22. Thus for some chemicals, both k_{EN} and k_{SN} (latter is neutral substitution process) must be known to estimate a value of k_N. The possibility of two competing hydrolysis pathways for polychlorinated ethanes, then is a good example demonstrating that rate constants and knowledge of molecular structure in themselves are not sufficient for establishing an SAR, but that some knowledge of the mechanism of the process is also required.

21.2 Limitations of Method

The main limitations for establishing SARs for k_N is the lack of accurate values of k_N for some of classes of chemicals and a lack of information on the mechanism of the neutral hydrolysis processes. Where qualitative SARs are available, as for epoxides and alkyl halides, their use is somewhat limited because the effect of many possible substituents cannot be assessed except in a general way; for instance, chlorination of the epoxide ring (i.e., R = Cl) in Table 21.2 will slow hydrolysis by the neutral process if water is acting as an acid, but the electron-withdrawing effect of Cl may enhance nucleophilic attack of water to break the C-O bond. As discussed above, from our recent results with hydrolysis of chlorinated ethanes we found that extensive chlorination may decrease the rate of substitution (exchange of Cl for OH), but may increase the rate of the elimination process.

21.3 Recommendations

More accurate data for k_N and better understanding of the mechanism of the pH-independent hydrolysis process are necessary for developing SARs for estimating values of k_N. Classes of chemicals of interest to EPA and that undergo neutral hydrolysis need to be identified; anhydrides, alkyl halides, isocyanates, and esters are primary candidates for study. Testing of SARs for k_N does not appear to be important at this time because the data base is not well established in terms of the structural variations required for a comprehensive SAR.

21.4 References

Mabey, W. R., and V. P. Barich. 1982. Unpublished results.

Mill, T., W. R. Mabey, J. S. Winterle, J. E. Davenport, V. P. Barich, D. E. Dulin, D. S. Tse, and G. Lee. 1982. Design and Validation of Screening and Detailed Methods for Environmental Processes. Final Report, EPA Contract No. 68-01-6325.

22 BASE-PROMOTED HYDROLYSIS RATE CONSTANT, k_B

The value of k_B is used to calculate k_h as discussed in Section 19. Base-promoted reactions (i.e., reactions with hydroxide ion) are important processes for many organic esters and may be important at pHs as low as pH 5-7 for some chemicals.

22.1 Estimation Methods

There is a large body of data on the base-promoted hydrolysis of organic chemicals, and the mechanisms of some of these processes are reasonably well understood. From this knowledge, several SARs are available for estimating k_B values. Values of k_B are also available for many chemicals for which no quantitative SARs are available, and these data can be included in an qualitative SAR format that is valuable for showing qualitative trends in k_B values with structure or for assigning k_B values by analogy. Several SARs for k_B values are shown in Tables 22.5 through 22.8, and follow the same form as those presented and discussed for k_A value estimations (see Section 19).

In recent work we have developed or tested quantitative SARs for k_B for several classes of chemicals (Mill et al., 1982a). Wolfe et al. (1978) reported k_B SARs for four classes of carbamates (Table 22.1), relating k_B to the pK_A of the leaving phenol group according to the equation shown in the table. To test the SAR for carbamates of structure IV, we measured k_B for the carbamate where X = p-CH_3. The measured value of k_B was 0.49 M^{-1} s^{-1}, which is compared with a value of 1.3 M^{-1} s^{-1} calculated from the SAR. These values were found to be in total agreement after analysis of the error in each value.

We also have developed and tested a k_B SAR for hydrolysis of the ethyl esters of aliphatic carboxylic acids using literature data for 9 esters (Table 22.2) to give a k_B SAR in the form of a Taft equation

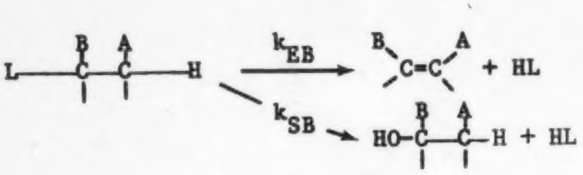
$$\log k_B = (2.53 \pm 0.16)\sigma^* + (1.11 \pm 0.23)E_s - 0.72 \qquad (22.1)$$

where σ^* and E_s are the polar substituent constant and steric substituent constants of Taft (Wiberg, 1964). This SAR was tested by measuring a k_B value for ethyl α-bromopropionate ($CH_3CHBrCO_2Et$); the measured value of $(10.1 \pm 0.1)\ M^{-1}\ s^{-1}$ is in good agreement with a calculated value of $15\ M^{-1}\ s^{-1}$ from equation (22.1) after analysis of error in each value. We also have developed a k_B SAR in the form of a Hammett equation for hydrolysis of ethyl esters of substituted benzoic acids using k_B data for four esters that were studied in our laboratory (Table 22.3).

$$\log k_B = (1.75 \pm 0.02)\sigma - 1.50$$

In other work at SRI we have found that for some polyhalogenated ethanes hydrolytic elimination may compete with the more useful substitution process. Mill et al. (1982b) found that hydrolysis of 1,1,1-trichloroethane was independent of pH in the range pH 3 to 11. In preliminary studies to assess the hydrolytic reactivity of other polychlorinated ethanes, Mabey and Barich (1982) found the hydrolyses were more rapid at pH 11 than at the lower pHs (see Table 22.4 for half-life data). These data suggest that a base- catalyzed process is dominant for some of these chemicals in the higher pH experiments. Most important, the presence of trichloroethylene as a product for two of the chemicals indicates that a base-promoted elimination process is occurring instead of the substitution process that is usually encountered in hydrolysis (e.g., substitution of Cl by OH to produce the alcohol product). The elimination reaction for this set of chemicals is probably caused by chloride substituents on the carbon bearing a hydrogen (carbon is referred to as an α-carbon) increasing the acidity of the hydrogen via the electron-withdrawing electronic effect of Cl-; the presence of chlorine substituents on the adjacent carbon (called the β-carbon) also probably increases the acidity of the α-hydrogen, but much less so than the substituent effect.

These results, as well as literature data obtained in different solvent systems (Hine, 1962), indicate that for some chemicals SARs for estimation of k_B should include elimination processes (rate constant k_{EB}) as well as substitution processes (rate constant k_{SB}).



$$k_B = k_{EB} + k_{SB}$$

Although very few data obtained in pure water solvent are available for estimating k_{EB} values from structural information, the possibility of elimination being an important process can be readily identified by the following rule:

Elimination may be important if

1. A = NO_2, Cl, CN, C(O)OR, C(O)R, $S(O_2)R$, S(O)R or other electron-withdrawing groups
2. B = Cl, Br, I, O(O)C-, or other good leaving groups.

It is obvious that such rule is readily used because elimination requires these specific activating and leaving groups on adjacent carbons.

22.2 Limitations of Method

Although a large amount of k_B data are available, some gaps exist for certain structural features that would make k_B SARs more general and applicable. As for other SARs for predicting the reactivity of chemicals, lack of convincing information on the mechanism of processes limits the development of many SARs, as does the meager data base for some classes of chemicals. SARs for k_B are available for ester and carbamate hydrolyses, and these can be used with some confidence.

22.3 Recommendations

Gaps in the k_B data base need to be filled for some classes of chemicals where the mechanism of the reaction can be reasonably assumed; in some cases it will certainly be found that a mechanism may be more complicated than anticipated. The classes of chemicals of greatest interest to EPA program offices need to be identified; isocyanates, alkyl halides, phosphorus esters, and various types of thioesters are among the classes of chemicals that will probably have priority for study. Testing of k_B SARs should not have priority over expansion of the data bases to include specific k_B values; development of qualitative SARs for k_B should have a high priority to determine the feasibility and utility of such systems in the fate assessment process.

22.4 References

Hine, J. 1962. Physical Organic Chemistry. McGraw-Hill, New York.

Kirby, A. J. 1972. In: Comprehensive Chemical Kinetics, Vol. 10, C. H. Bamford and CFH Tipper, Ed. Elsevier, New York.

Mabey, W. R., and T. Mill. 1978. Critical Review of Hydrolysis of Organic Compound in Water Under Environmental Conditions. J. Phys. Chem. Ref. Data 7:383.

Mabey, W. R., and V. P. Barich. 1982. Unpublished results.

Mill, T., J. S. Winterle, J. E. Davenport, G. C. Lee, W. R. Mabey, V. P. Barich, W. Harris, D. Ingersoll, and R. Bawol. 1982a. Validation of Estimation Techniques for Predicting Environmental Transformation of Chemicals. Final Report, EPA Contract 68-01-6269.

Mill, T., W. R. Mabey, J. S. Winterle, J. E. Davenport, V. P. Barich, D. E. Dulin, D. S. Tse, and G. Lee. 1982b. Design and Validation of Screening and Detailed Methods for Environmental Processes. Final Report, EPA Contract No. 68-01-6325.

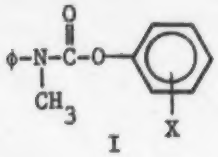
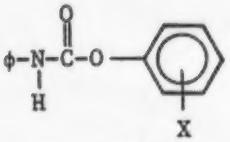
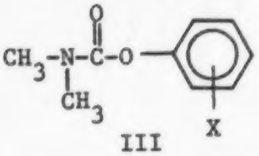
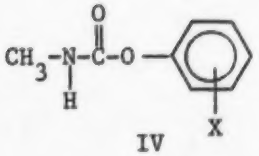
Wiberg, K. B. 1964. Physical Organic Chemsitry. John Wiley and Sons Inc., New York.

Wolfe, N. L., Zepp, R. G., and D. F. Paris. 1978. Use of Structure-Reactivity Relationships to Estimate Hydrolytic Persistence of Carbamate Pesticides. Water Res. 12:421.

Table 22.1

SARs FOR AROMATIC CARBAMATES[a]

$$\log k_B = -\rho \; pK_A + C$$

Structure	$-\rho$	C
 I	0.26 ± 0.001	-1.3 ± 0.1
 II	1.15 ± 0.02	13.6 ± 0.2
 III	0.17 ± 0.04	-2.6 ± 0.4
 IV	0.91 ± 0.03	0.3 ± 0.4

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[a] From Wolfe et al. (1978).

Table 22.2

k_B DATA FOR ETHYL ESTERS OF ALIPHATIC ACIDS (RC(O)OEt)[a]

R	k_B[a] (M^{-1} s^{-1})	Log k_B	σ^*[b]	E_s[b]
CH_3	0.111	-0.954677	0.0	0.0
CH_3CH_2	0.087	-1.066481	-0.1	-0.07
$CH_3CH_2CH_2$	0.0383	-1.416801	-0.115	-0.36
$ClCH_2$	33.2	1.521138	1.05	-0.24
$BrCH_2$	49.7	1.696356	1.0	-0.27
ICH_2	16.2	1.209515	0.85	-0.37
Cl_2CH	677.0	2.830589	1.94	-1.54
Cl_3C	2570.0	3.409933	2.65	-2.06
F_2CH	4500.0	3.653213	2.05	-0.67

---

[a] Kirby (1972), unless otherwise noted.

[b] σ^* and E_s values are listed in most physical organic chemistry textbooks; see Wiberg (1964).

[c] Mabey and Mill (1978).

Taft equation for k_B:

$$\log k_B = (2.53 \pm 0.16)\sigma^* + (1.11 \pm 0.23)E_s - 0.72$$

Table 22.3

k_B VALUES FOR HYDROLYSIS OF p-X-$C_6H_4CO_2Et$ AT 25°C IN WATER

X	σ_X	k_B (M^{-1} s^{-1}) x 10^2	log k_B
$-NH_2$	-0.660	0.229	-2.64
-H	0	3.00[a]	-1.52
-F	0.062	3.89	-1.41
$-NO_2$	0.778	74.9	-0.125

---

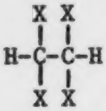
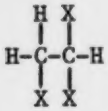
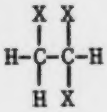
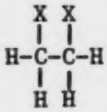
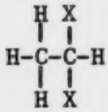
[a] A value of 3.0 x 10^{-2} M^{-1} s^{-1} at 25°C has been reported (Mabey and Mill, 1978).

Hammett equation for k_B:

$$\log k_{B(x)} = (1.75 \pm 0.02)\sigma - 1.50$$

Table 22.4

PRELIMINARY RESULTS OF POLYCHLOROALKANE HYDROLYSIS STUDIES (X = Cl)

Compound	$t_{1/2}$ at pH 11, 25°C	$t_{1/2}$ at Lower pH
 $\mathrm{H{-}\overset{X}{\underset{X}{C}}{-}\overset{X}{\underset{X}{C}}{-}H}$	96 min (TCE is a product)	7.5 h at 55°C, pH 7 (TCE is a product)
 $\mathrm{H{-}\overset{H}{\underset{X}{C}}{-}\overset{X}{\underset{X}{C}}{-}H}$	1.7 d	68 d at 80°C, pH 5
 $\mathrm{H{-}\overset{X}{\underset{H}{C}}{-}\overset{X}{\underset{X}{C}}{-}H}$	8.1 d (TCE is a product)	165 d at 80°, pH 5
 $\mathrm{H{-}\overset{X}{\underset{H}{C}}{-}\overset{X}{\underset{H}{C}}{-}H}$	44 d	28 d at 80°, pH 5
 $\mathrm{H{-}\overset{H}{\underset{H}{C}}{-}\overset{X}{\underset{X}{C}}{-}H}$	260 d ($^{-}$OAc + 3 Cl^{-} are products)	7 h at 75°, pH 5

TCE = Trichloroethylene

Table 22.5

SAR FOR k_B: ALIPHATIC ESTERS AT 25°;[a]

VARIATION OF $R\overset{O}{C}-OR$

$R-\overset{O}{C}-OR'$				
R	R'	Range of k_B	Range of R	
H	n-Alkyl	36-22	--	
n-Alkyl	n-Alkyl	0.11-0.04*	Me to nPr	(3)[c]
$X_n-CH_{3-n}-$ x = halide	n-Alkyl	36-12,800*	$ClCH_2$ to Cl_2CH	(5)
Vinyl	n-Alkyl	0.064-0.15	CH_2CH- to $CH_3C=CH-$	(3)
Alknyl	n-Alkyl	0.57-4.7	$HC\equiv C-$ to $CH_3C\equiv C-$	(2)

---

[a] Reference: Mabey and Mill, 1978.
[b] Quantitative SAR available for Et ester (see Table 22.2).
[c] Number in parentheses is number of chemicals in data base.

Table 22.6

SAR FOR k_B: ALIPHATIC ESTERS AT 25°C[a]

RCO_2R'		Range k_B (M^{-1} s^{-1})	Range of R'	
R	R'			
CH_3	n-Alkyl[a]	0.18-0.06	CH_3 to nBu	(4)[b]
CH_3	s-Alkyl	0.026-0.017	iPr to cyclo C_5H_9	(3)
CH_3	t-Alkyl	0.0015	t-Bu	(1)
CH_3	Allyl	See 1°, 2°, 3° effect		(2)
CH_3	Vinyl	10-0.8, steric effects important		(2)
CH_3	xC_6H_4-	1.4-94	x=H to 2,4,-diNO_2	(2)

---

[a] Mabey and Mill, 1978.
[b] Number in parentheses is number of chemicals in the data base.

Table 22.7

SAR FOR k_B: ALIPHATIC AMIDES AT 25°C

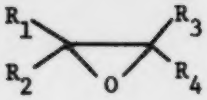
$R_1CONR_2R_3$				
R_1	R_2	R_3	Range k_B (M^{-1} s^{-1})	Range of R
Alkyl[a]	H	H	1.77-17	1°, 2°, 3° alkyl(8)[b]
x_nCH_{3-n} (x = halide)	H	H	1400-135000	$ClCH_2$ to Cl_3 (3)
CH_3	Alkyl	H	0.367-3.58	CH_3 to iPr (3)
CH_3	Alkyl	Alkyl	5.18-0.12	CH_3 to Et (3)

---

[a] Underlined R is the varied group in the last column.
[b] Number in parentheses is the number of chemicals in the data base.

Table 22.8

SAR FOR k_B: EPOXIDES AT 25°C
VARIATION OF R_n



R_1, R_2 R_3 R_4	Range of 10^4 k_B (M^{-1} s^{-1})	Range of R
Alkyl, H (noncyclic)	1.0-0.65	Me, H (3)[a]
Alkenyl, H (cyclic)	14.8	Cyclo-2-hexenyl (1)

---

[a] Number in parentheses is the number of chemicals in the data base.

23 DIRECT PHOTOLYSIS RATE CONSTANT, k_p

Direct photolysis rate constants are used to predict transformation rates of chemicals that directly absorb light and then undergo reaction. The values of k_p that are currently estimatable are for chemicals in dilute, weakly absorbing solutions of chemical, and these values can be corrected for light attenuation in the natural water of interest. Light absorption and scattering due to dissolved and particulate matter will significantly reduce the overall effective photolysis rate constant in a natural water.

23.1 Estimation Method

The direct photolysis rate constant, k_p, may be calculated from the more fundamental chemical parameters of the reaction quantum yield ϕ and the absorption coefficient ε_λ using the equation

$$k_p = \phi b \Sigma \varepsilon_\lambda I_\lambda = \phi b k_a \quad , \qquad \text{where } k_a = \Sigma \varepsilon_\lambda I_\lambda \qquad (23.1)$$

where I_λ is the photon flux in the wavelength region λ, b is a constant for conversion of units, and k_A is a rate constant for light absorption by chemicals. The calculation of k_p is discussed in detail by Zepp and Cline (1977) and Mabey et al. (1982). SARs and rules for estimation of ϕ, k_a, or ε_λ are discussed in Sections 24 and 25. Except for a data base included in an SAR system that may serve as a compilation of photolysis rate constant data or half-lives for reference, an SAR for direct estimation of k_p from structural features of a molecule is not possible (see Sections 24 and 25).

23.2 Limitations of Method

A data base for k_p values as part of an SAR system may be useful for determining whether direct photolysis may be an important process;

such a data base would include a list of half-lives for chemicals at particular latitudes and seasons when information is available. A simplified version of SOLAR (Zepp and Cline, 1978) may be useful in an estimation system for providing k_p values if ϕ and ε_λ data are available. At present, a maximum value of k_p can be estimated if it is assumed that $\phi = 1$, which is the maximum value that can be expected for photolysis of dilute chemical in pure water.

23.3 Recommendations

We recommend priority should be given to development of SARs and rules for estimating values of ϕ and ε_λ that can be used in assessments rather than presentation of data for k_p.

23.4 References

Mabey, W. R., T. Mill, and D. G. Hendry. 1982. Test Protocols for Environmental Processes: Photolysis in Water. EPA Report (Draft). EPA Contract No. 68-03-2227.

Zepp, R. G., and D. M. Cline. 1977. Rates of Direct Photolysis in Aquatic Environments. Environ. Sci. Technol. 11:359-366.

24 PHOTOLYSIS REACTION QUANTUM YIELD, ϕ_r

The direct photolysis reaction quantum yield ϕ_r is used to calculate the direct photolysis rate constant (see Section 23). ϕ_r is a measure of the efficiency of the chemical for conversion of absorbed light into chemical reaction and is expressed in terms of the moles of chemical reacted per Einstein of light absorbed by the chemical. The maximum quantum yield for direct photolysis processes in aqueous systems is unity. As discussed below, the processes determining ϕ_r values are complex, and the unknown or uncertain effects of molecular structure on the various competing processes makes a reliable estimate of ϕ from structure difficult unless the particular photolysis mechanism is known.

24.1 Estimation Method

One of the principal difficulties in estimating a reliable value of ϕ_r based on the structure of a molecule is the lack of information on the probable pathway for the photoreaction. Sunlight photochemical reactions occur by way of excited state species with some 50 to 100 kcal excess energy above that of their ground state forms. As a result, these molecules have available to them multiple channels for reaction (e.g., rearrangement, dissociation), many of which are not directly accessible from the ground state because of spin or energy restrictions (Turro et al., 1978, discuss spin effects). Thus, the ability to compare the same reaction pathway among a set of structural variations—which is a cardinal rule for using SAR reliably— often cannot be followed. This problem, as well as other difficulties, is demonstrated by reference to Table 24.1.

In Table 24.1, the simplest sequence of processes that would result in loss of chemical C are those involving the singlet excited state $^1C^*$ shown in processes 1 through 5; the reaction quantum yield is determined by the expression

$$\phi_r = R5/(R2 + R3 + R4 + R5)$$

Table 24.1

GENERAL PHOTOLYSIS PROCESSES

$C \xrightarrow{h\nu} {}^1C^*$	(1)	Excitation to singlet state.
${}^1C^* \longrightarrow C$	(2)	Decay to ground state.
$Q + {}^1C^* \longrightarrow C + {}^1Q^*$	(3)	Quenching of singlet state.
${}^1C^* \longrightarrow {}^3C^*$	(4)	Intersystem crossing to triplet state.
${}^1C^* \longrightarrow \text{Product}$	(5)	Product formation.
${}^3C^* \longrightarrow C$	(6)	Decay to ground state.
$Q + {}^3C^* \longrightarrow C + {}^3Q^*$	(7)	Quenching of triplet state.
$R + {}^3C^* \longrightarrow \text{Product}$	(8)	Product formation, rxn with reactant R.
${}^3C^* \longrightarrow \text{Product}$	(9)	Product formation.

where R represents the rate of the particular process. If R5 is much more rapid than all other processes, then $\phi_r = 1$. If competing processes are faster, then $\phi \ll 1$, and the influence of structural changes on ϕ may be masked by structural effects on the competing processes. Furthermore, processes (2) and (3) do not lead to transformation, and reaction (4) leads to the triplet excited state species, which may undergo different reactions than the singlet species. One example of how structure may affect a reaction quantum yield may be found in the effect of bromide and iodide substituents on aromatic structures, where the presence of these atoms is well-known to facilitate intersystem crossing of the singlet state to the triplet state [process (4)]; such an effect may decrease ϕ for chemicals undergoing photoreactions occurring via the singlet state if halogenated structures are compared to structures without these halide substituents, and possibly increase ϕ for reactions occurring via a triplet state (see below).

Table 24.1 also shows the processes which may be important for transformation reactions occurring from the triplet excited state ($^3C^*$) [processes (8) and (9)]. Obviously, the expression for the ϕ_r becomes more complex for these reactions, with process (4) being critical in determining whether a reaction occurs from a singlet or triplet excited state. Given that the processes leading to photoreactions are complex, it is evident that estimation of ϕ values by simple analogy to chemical structures that appear to be similar is subject to error, which may not be easily identified without some knowledge of a reaction mechanism and possible structural influences on the competing processes.

Table 24.2 lists reaction quantum yields measured in water for several classes of chemicals. The data sets for polycyclic aromatics and nitroaromatics show ϕ values thath range over an order of magnitude for each class. These quantum yields are not as diverse as might be expected from the complex set of processes shown in Table 24.1, but then the structural variations considered for these classes are not great.

Table 24.2

REACTION QUANTUM YIELDS FOR SELECTED CLASSES OF CHEMICALS

Chemical Class	ϕ	Reference
Chlorobenzenes	> 0.1	Unpublished work, SRI.
o-Chlorobephenyl, terphenyls	> 0.1	Unpublished work, SRI; Chittim et al. (1978)
p-Chlorobiphenyl, terphenyls	< 0.01	Chittim et al. (1978).
o-Nitrotoluenes	$(4.0-67) \times 10^{-4}$	Unpublished work, SRI.
Nitrotoluenes	$(<4-158) \times 10^{-4}$	Unpublished work, SRI.
Polycyclic aromatics[a]	$(15-0.5) \times 10^{-3}$	Zepp and Schlotzhauer, (1979); Mill et al.
(1981).		
Aromatic ketones		
α-cleavage	~ 0.3 to 0.001	(see text)
β-cleavage	~ 1.0	(see text)
Aliphatic ketones	0.3 to 0.001	(see text)

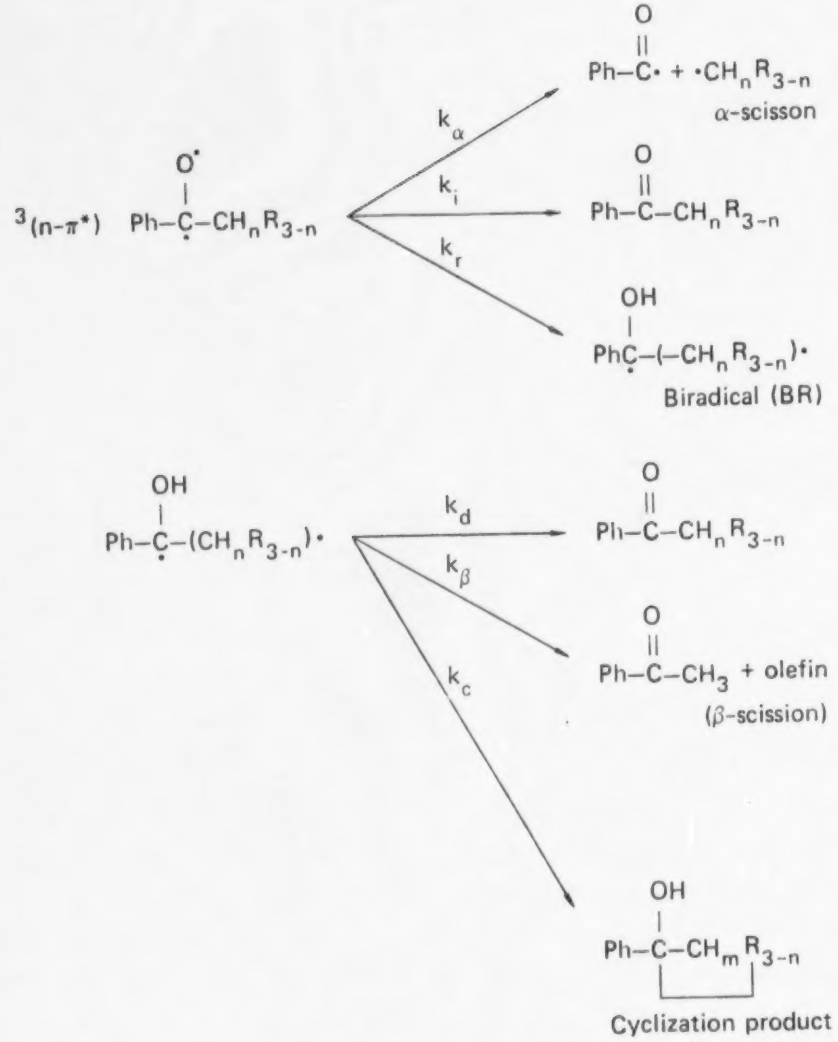
---

[a] Excluding data for fluoranthene (see Zepp and Schlotzhauer, 1979).

Although these data can provide a general guide to ϕ values for a class of chemicals, the application to a specific chemical cannot be done reliably.

An example of a useful SAR for photolysis is that for the photolysis of arylalkyl ketones to give acetophenone and an alkene, which occurs via a biradical intermediate (BR). A simplified photokinetic scheme for arylalkyl ketones is shown in Figure 24.1, where the reaction quantum yield, ϕ_{II}, is determined in part by the competing pathways controlling the fate of the intermediate BR. Polar solvents such as alcohols stabilize the BR intermediate and eliminate the back reaction (k_d), and in most cases ϕ becomes 1.0; in organic solvents, however, ϕ_{II} is generally closer to 0.3-0.4 because of competitive reversion to ketone (k_d) (Wagner and Kemppainen, 1968; Turro et al., 1978). In water ϕ may be much lower.

Table 24.3 lists the ϕ values for some aromatic ketones that undergo either α- or β-cleavage, thus fulfilling the requirement that similar pathways must be compared to develop an SAR. The immediate conclusion is that in α-cleavage, the order of reactivity (as determined by ϕ values) follows the intuitive order expected for faster cleavage for more stable radicals (Walling, 1957). Thus, t-Bu and $PhCH_2$ are more stable than Me. The strong inhibiting effect of p-Ph on t-Bu cleavage cannot be simply a substituent effect but must reflect a change in competition among pathways; in this case probably faster loss of energy back to ground state. In β-cleavage, however, the situation clearly is more complicated and, among butyrophenones, substituents that are both electron donating and withdrawing can facilitate or inhibit cleavage but effects are small. The striking effect of the p-NH_2 or o-OH (not shown) probably reflects a change from one kind of triplet state to another. The data compiled in Table 24.3 were measured in organic solvents without air. In aerated water we would expect some reduction in α-cleavage values and significant decreases in β-cleavage values (see above).


$^3(n\text{-}\pi^*)$
Ph–C–CH$_n$R$_{3-n}$
k_α
k_i
k_r
α-scisson
Biradical (BR)
k_d
k_β
k_c
(β-scission)
olefin
Cyclization product

$$\phi_\beta = \phi_{BR}\phi_p$$

$$= \frac{k_r}{k_r + k_i} + \frac{k_s}{k_s + k_c + k_d}$$

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Figure 24.1 Photolysis of ketones.

Table 24.3

QUANTUM YIELDS FOR PHOTOLYSIS OF KETONES AT 25°C

Ketone	Solvent[a]	ϕ[b]
α-Cleavage	Or	
PhCOMe		< 0.01
PhCOt-Bu		~ 0.3
$PhCOCH_2Ph$		~ 0.4
4-MeOPhCOt-Bu		~ 0.1
4-PhPhCOt-Bu		<0.001
β- Cleavage		
$PhCO(CH_2)_2Me$	Or	0.36
$PhCO(CH_2)_2Me$	Al	1.0
$PhCOCHMe_2$	Or	0.36
$PhCO(CH_2)_2$-i-Pr	Or	0.25
$PhCO(CH_2)CH(Me)OMe$	Or	0.21
$PhCO(CH_2)_3CO_2Me$	Or	0.46
$XPhCO(CH_2)_3Me$	Or	
X = H		0.42
X = p-MeO		0.10
X = p-MeO		0.014
X = p-Me		0.39
X = p-F		0.29
X = $p-NH_2$		0.00

---

[a] Or = nonpolar organic solvent,
Al = alcohol.

[b] Quantum yield in deaerated system.

These results and others like them lead us to conclude that future studies that would assist in developing a reliable data base for estimating ϕ values first must demonstrate that the chemicals of interest are photolyzing in the same way and through the same intermediates.

Until substantially more studies of these kind are undertaken our ability to estimate ϕ for use in estimating k_p in aquatic environment will remain very limited. However, in the near term, ϕ value measurements in aerated water for important classes of photoactive chemicals will remain a valuable short term objective. Often, as we have seen with nitroaromatics and chloroaromatics (Table 24.2) very useful generalizations are possible without extensive knowledge of mechanism and pathway. In the longer term, however, better understanding of the mechanistic features of these processes, including theoretical studies, are essential for significant progress in developing SARs for photolysis.

24.2 Limitations of Method

Development of reliable SARs for estimating reaction quantum yields requires information on the specific pathways responsible for photoreactions as well as on the energy transfer and decay processes that influence the rate of photoreaction. As discussed above, lack of knowledge on how structure influences these process limits estimation of ϕ values. A maximum value of k_p can be estimated if $\phi = 1$ is assumed; this is a reliable value because $\phi = 1$ is the maximum limit expected for photolysis of a dilute chemical in aqueous solution. Given the uncertainty in predicting ϕ, no lower error limits can be estimated for any k_p value. If the maximum values of k_p indicates that photolysis is not important compared to other processes, then photolysis can be reliably neglected in subsequent assessments. In the short term, a data base of ϕ data and other information (including product and mechanistic information) may serve as useful generalizations for estimating ϕ values.

24.3 Recommendations

Studies that permit classification of chemicals by common reaction pathways need to be performed before useful SARs for predicting ϕ can be developed. These studies involve both literature review and laboratory measurements to test mechanistic hypotheses and fill data gaps. In the short term, reaction quantum yields of chemicals measured in aqueous solution will be useful in establishing general rules and limits that can be used in some assessments.

24.4 References

Chittim, B., S. Safe, N. J. Bunce, L. O. Ruzo, K. Olie, and O. Hutzinger. 1978. The Photolysis of Chlorinated p-Terphenyls. Can. J. Chem. 56:1253-1260.

Mill, T., W. R. Mabey, B. Y. Lan, and A. Baraze. 1981. Photolysis of Polycyclic Aromatic Hydrocarbons in Water. Chemosphere 10(11/12):1281-1290.

Turro, N. J., V. Ramamurthy, W. Cherry, and W. Farneth. 1978. Effect of Wavelength on Organic Photoreactions in Solution. Chem. Rev. 78:125-144.

Wagner, P. J., and A. E. Kemppainen. 1968. Is There Any Correlation Between Quantum Yields and Triplet-State Reactivity in Type II Photoelimination? J. Am. Chem. Soc. 90:5896-97.

Walling, C. 1957. Free Radicals in Solution. John Wiley and Sons, New York.

Zepp, R. G., and P. F. Schlotzhauer. 1979. "Photoreactivity of Selected Aromatic Hydrocarbons in Water." In: Polynuclear Aromatic Hydrocarbons, P. W. Jones, and P. Leber, Eds. Ann Arbor Science, Ann Arbor, MI.

25 MOLAR ABSORPTION COEFFICIENTS, ε_λ

Values of ε_λ at specific wavelength in the solar spectral region (wavelengths above 290 nm) are used to calculate the direct photolysis rate constants of chemicals in pure water (see Section 23).

25.1 Estimation Method

Mabey et al. (1982) have shown that chemicals with even minimal light absorption above 290 nm may undergo direct photolysis if reaction quantum yields are near unity. Thus, a hypothetical chemical with absorption coefficients of greater than 0.1 M^{-1} cm^{-1} in the region 290 to 360 nm would have a 12-day half-life at 40° latitude in summer if $\phi = 1$; if the absorption coefficients were 0.1 M^{-1} cm^{-1} out to 320 nm, the half-life would be 120 days for the same season and latitude. Some SARs for estimating values of ε_λ are thus useful for determining whether a chemical may absorb sunlight.

Some generalizations about the relationship between structure and the light-absorbing properties of these structures are listed in Table 25.1, and such information can serve as a first screening level to determine whether direct photolysis can be important. These data, and ready access to spectrophotometers which easily produce good ultraviolet/visible spectra, may negate a need to further estimate spectral properties of chemicals more precisely if laboratory facilities and a particular chemical are available.

If no facilities for obtaining necessary spectra are available and it is determined that more precise absorption spectra data are necessary for evaluating the rate constant for direct photolysis, a second SAR for estimating the rate constant for light absorption k_a may be useful. Since discrete ε_λ values over all wavelengths are of no particular interest except for calculating k_a (via $\Sigma\varepsilon_\lambda I_\lambda$ as discussed in Section 23), an SAR listing k_a values for some selected model chemicals may be useful for some assessment purposes. The k_a values could be listed for

Table 25.1

APPROXIMATE ABSORPTION REGIONS FOR ORGANIC MOLECULES

Class	Example	Region nm	Reference
Aliphatics[c]			
Hydrocarbons	$n\text{-}C_4H_{10}$	120-170	a
Fluorides, chlorides bromides	$CHBr_3$, $CHCl_3$	180-260	a, b
Iodides	C_3H_7I	180-320	b
Ethers, alcohols	C_2H_5OH, $C_2H_5OC_2H_5$	150-200	a
Aldehydes	CH_3CHO	240-340	a
Ketones	$C_2H_5C(O)CH_3$	240-320	a, b
Acids	$CH_3C(O)O$	200-230	a, b
Esters	$CH_3C(O)OCH_3$	200-240	a
Amides	$C_2H_5C(O)NHt_2$	180-220	a, b
Amines	$(C_2H_5)_3N$	180-240	a, b
Azines	$(CH_3)_2C{=}N{-}N{=}C(CH_3)_2$	200-290	b
Azo	$CH_3{-}N{=}N{-}CH_3$	200-230, 320-400	a
Nitro	CH_3NO_2	200-220, 260-320	a, b
Nitroso	$(CH_3)_3CNO$	200-300, 540-740	a
Nitrite	$(CH_3)_3CONO$	200-240, 320-400	a, b
Nitrate	$C_2H_5ONO_2$	200-300	a
Sulfide	$C_2H_5SC_2H_5$	200-220	a, b
Disulfide	CH_3SSCH_3	200-240	a, b
Nonconjugated[c] Olefinics and Acetylenes			
Hydrocarbons	$(CH_3)_2C{=}C(CH_3)_2$	170-240	a, b
Aldehydes	$CH_2{=}CHCHO$	200-250, 290-400	b
Ketones	$CH_3CH{=}CH{-}C(O)CH_3$	200-240, 260-330	b
Nitro	$CH_3C(NO_2){=}C(CH_3)_2$	180-380	b

Table 25.1 (concluded)

Aromatics			
Benzene	Benzene	200-280	a
Alkylbenzenes	Toluene	200- > 280	a
Halobenzenes	Cl- or Br-benzene	200-280	a
Nitrobenzenes	Nitrobenzene	200-300	a
	Trinitroluene	200-450	d
Aminobenzenes	Aniline	200-3300	a
Azobenzene	Azobenzene	< 200- > 500	a
Phenols	Phenol	200-305	a
Vinylbenzenes	Styrene	200-300	a
	Stilbene	200-330	a
Acids	4-nitrostilbene	200-390	a
	Benzoic acid	200-300	a
Carbonyls	Benzaldehyde	200-375	a
	Benzophenone	200-410	a
Polycyclic aromatics	Napthalene	200-325	a
	Anthracene	200- > 400	a
	Phenanthrene	200-380	
	Benzo[a]pyrene	200-410	e
Heteroaromatics	Quinoline	200-360	e
	Benzoquinoline	200-380	e
	9H-Carbazole	200-390	e
	Benzo[b]thiophene	200-312	e

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[a] Calvert and Pitts (1967).
[b] Perkampus (1971).
[c] Hendry and Kenley (1979).
[d] Spanggord et al. (1979).
[e] Mill et al. (1981).

the summer and winter solstices to estimate maximum and minimum rate constant values. The rate constants k_a could be used in either of two ways:

(1) The system user could assume reaction quantum yield of 1.0, and k_a would then be a maximum direct photolysis rate constant for the chemical. If this photolysis rate constant indicates that photolysis may be important, the user would then need to obtain better values of ε_λ from another source (preferably measurements).

(2) A ϕ value of the system users choice could be multiplied by k_a to get a rate constant k_p for use in the assessment. The SAR for estimating k_a would be approached by the user in the following sequence:

A. Select a model chemical in the SAR that is most similar to the chemical of interest. This selection could be based on a qualitative consideration of structural and chromophore similarities. It also is possible to estimate an ε_λ value at several wavelengths from a literature spectrum although the spectrum cannot be resolved well enough to get all the ε_λ values needed for calculation of k_a or k_p. If the ε_λ values estimated from the spectra at selected λ values match at those for the model chemical, then the k_a for the model chemical may suffice for estimation of k_a for the chemical of interest.

B. The product of k_a and ϕ would then give k_p.

The last SAR is not currently available and would require a significant amount of effort to select model chemicals, measure uv spectra, and calculate k_a values.

25.2 Limitations of Method

The estimation of ε_λ is currently limited to determining whether or not a chemical absorbs sunlight. This is often difficult for chemicals that have weak tailing absorptions into the solar spectral region (above 290 nm). Direct measurement of ε_λ is the only source of reliable ε_λ data for use in estimating k_p.

25.3 Recommendations

Because no procedures for estimating accurate ε_λ values are available, we suggest that a SAR system be set up for first estimating whether a chemical may absorb sunlight, and if so, an SAR be developed that estimates k_a values by analogy to model chemicals. It may be possible to have the ε_λ values of the model chemical matched to those of particular chemicals by computer, which would facilitate the use of the ε_λ/k_a SAR system. More accurate ε_λ for a variety of chemicals is needed to develop and test this approach to estimating ε_λ/k_a values.

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26 OXIDATION BASE CONSTANTS IN AIR AND WATER, k_{ox} (RO_2 and $^1O_2$ in water, •OH in air)

Many chemicals can and do undergo oxidation in water and air by several different pathways and with different oxidants. In water the principal oxidants are peroxy radicals RO_2 and singlet oxygen $^1O_2$; in air the principal oxidant is HO radical. A few very reactive olefins also oxidize with ozone in air rapidly enough to make this an important pathway. All of the oxidants are formed by interaction of sunlight with natural or anthropomorphic chemicals found in water and air including urban smog. Oxidation processes important in the environment and their SARs have been reviewed by Mill (1979, 1980) and Hendry and Kenley, (1979). SARs for oxidation of organic chemicals are well developed because of extensive data bases for oxidation rate constants for these major oxidants (Howard, 1972, Hendry, et al., 1975).

26.1 Estimation Methods

Oxidation by RO_2•. The range of measurable reactivities of chemicals with RO_2 covers a range of 10^{10}, but only chemicals with rate constants $>10^3$ M^{-1} s^{-1} will oxidize in water at significant rates because the best estimate for the concentration of RO_2 in natural water places it at about 10^{-9}-10^{-10} M (Mill et al., 1980). Thus, a second-order RO_2 oxidation rate constant (k_{ox}) of 10^3 M^{-1} s^{-1} and a RO_2 concentration of 10^{-9} M would give an environmental oxidation rate constant (first-order constant) of 10^{-6} s^{-1}, which corresponds to a half-life of eight days. From known values of k_{ox} we can exclude from assessments oxidation of most chemicals and focus on the few extremely reactive classes.

Aromatic amines and phenols are two major classes of chemicals that are reactive enough toward RO_2• radical to warrant detailed consideration regarding SAR. Fortunately, because these compounds are useful as antioxidants, several investigators have measured absolute rate constants for H-atom transfer to $RO_2\cdot$ from many types of phenols and some amines (Howard and Ingold, 1963; Howard, 1972).

$$RO_2\cdot + XPhOH \xrightarrow{k_{inh}} RO_2H + XPhO\cdot$$

Table 26.1 summarizes the absolute rate constants (k_{inh}) and SARs for selected classes of phenols; values of ρ^+ for each subseries of phenols are also listed. In all cases ρ^+ is negative, indicating that the transition state has some positive character stabilized by electron donor substituents. The reactivity of all measured phenols ranges from a low of about 3×10^2 M^{-1} s^{-1} for 4-CNPhOH to a high of about 9×10^4 M^{-1} s^{-1} for k_{inh} for hydroquinone extrapolated to the same temperature.

Aromatic amines have been subjected to less systematic study than phenols; nonetheless, the data listed in Table 26.2 show that as a group, amines are as reactive or more so than phenols: values of k_{inh} range from a low of 9×10^2 M^{-1} s^{-1} for $MeO_2CPhNHMe$ to highs of 2×10^5 M^{-1} s^{-1} for diphenylamines. Values of ρ are negative and are similar to those for phenols (-0.8 to 0.6).

We have recently shown that substituted phenols oxidized by RO_2 in water at 25°C have nearly the same ρ^+ as in organic solvents (Winterle and Mill, 1982).

Oxidation by $^1O_2$. Zepp et al. (1978) demonstrated that sunlight irradiation of natural waters led to production of $^1O_2$ at average concentrations of 1×10^{-12} M. This value, when combined with rate constants for oxidation of a variety of organic structures, led to predictions of very long half-lives for most simple structures. Reactive molecules include electron-rich molecules such as branched olefins, eneamines, polycyclic aromatics, and sulfides.

SAR for $^1O_2$ oxidations are very limited. Foote and Denny (1971) measured the relative rates of oxidation of a series of substituted styrenes and found that for allylic oxidation correlation by the Hammett equation σ was satisfactory and $\rho = -0.92$. However, epoxidation of the styrene double bond that accompanies allylic oxidation is not correlated

TABLE 21

SRC FOR OXIDATION OF PENCLS BY $RO_2\cdot$ RADICAL IN SOLVENTS

Substituent X	$10^{-4}\ k_{inh}\ M^{-1}\ s^{-1}$
——XPhOH at 65°C with polystyrylperoxy radical[a]——	
4-HO	9.3
4-Me	0.92
H	0.23
3-Cl	0.056
4-CN	0.030
$\rho^+ = -1.49$ in styrene	
$\rho^+ = -3.7$ in chlorobenzene	
$\rho^+ = -3.48 \mp 0.114$ in methyl methacrylate	
——$2,6\text{-}(t\text{-}Bu)_2\text{-}4\text{-}X\text{-}PhOH$ at -37°C with $t\text{-}BuO_2\cdot$[b]——	
MeO	2.3
Me	0.50
H	0.34
Cl	0.50
CN	0.10
$\rho^+ = -1.00$, $r = 0.94$ in isopentane	
—o-Alkyl PhOH at 65°C with polystyryl peroxy radical[c]—	
$2,6\text{-}Me_2\text{-}4\text{-}XPhOH$	
Me	2.8
Cl	1.2
CN	0.73
H	0.89
$\rho^+ = -1.36 \mp -1.46 \pm 0.115$	

TABLE 21
(Concluded)

Substituent X	10^{-4} k_{inh} M^{-1} s^{-1}
2-t-Bu-n-XPhOH[c]	
H	0.75
4-MeO	10.7
5-Me	1.1
4-IN	0.087
	$\rho^+ = -1.46 \pm 0.012$
2,6-(t-Bu)$_2$-4-XPhOH[c]	
H	0.23
MeO	3.1
Me	0.80
Cl	0.32
CN	0.077
NO$_2$	∿ 0.05
	$\rho^+ = -1.11 \pm 0.026$

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[a] Howard and Ingold, 1963a.
[b] Howard and Furimsky, 1973.
[c] Howard and Ingold, 1963b.

TABLE 22

SRC FOR OXIDATION OF AMINES BY $RO_2\cdot$ RADICAL IN SOLVENTS

Amine	10^{-4} k_{inh} M^{-1} s^{-1}
N-Methylanilines at 65°[a,b]	
4-H	0.4
4-Me	1.2
3-Me	0.5
4-MeOC(O)	0.09
4-MeO	1.9
$\rho = -1.6$	
Diphenylamines at 65°[a,b]	
4,4′-H_2	4
4,4′-Me_2	10
4,4′-$(MeO)_2$	33
4,4′-$(NO_2)_2$	0.16
4-MeO	20
3-Cl	1.8
4-NO_2	0.6
$\rho^+ = -0.89$	
Napthylamines at 40°C[a,b]	
N-α-Napthyl	0.15
N-α-Naphthyl-N-Phenyl	1.25
N-β-Napthyl-N-Phenyl	10
N,N-Di-β-Napthyl	18

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a In reaction with poly(peroxystyryl)peroxy radical.
b From Brownlie and Ingold (1967).

well by either σ or σ^+, but is correlated by $[\sigma - 0.37 (\sigma^+ - \sigma)]$ to give $\rho = -0.87$. We have measured ρ for the same styrenes in water and found a similar relation (Winterle and Mill, 1982).

Oxidation by HO• Radical HO• radical is the most important oxidant in the atmosphere, and it reacts by H-atom transfer and addition to double bonds and aromatic rings. Detailed lists of rate constants are found in Hendry and Kenley (1979) and Hampson and Garvin (1977). Most organic molecules with -CH- or $-CH_2-$ bonds or aromatic structures react rapidly with half-lives of less than a day; highly halogenated chemicals (including Freons) are much less reactive.

The rate constant k_{HO} for oxidation of a specific structure can be estimated using the additivity procedure of Hendry and Kenley (1979), which, depending on the structure, requires estimation of the individual rate constants for H-atom transfer and addition. The expression for H-atom transfer is

$$k_{HO(H)} = \sum_i^n \alpha_i \beta_i k_i \qquad (26.1)$$

in which α_i and β_i are substituent constants and k_i is the rate constant for the i-$_{th}$ CH bond. Similar expressions have been developed for addition to double bonds and to aromatic rings. The probable error in values of k_{HO} estimated in this way is about a factor of two (± 100%). A listing of substituent constants is found in the report by Hendry and Kenley (1979). We have shown that the estimation method for k_{HO} gives excellent agreement with measured values (< factor of 2) for six aliphatic and aromatic chemicals tested (Mill et al., 1982).

Oxidations by Ozone. Ozone is a selective oxidant that reacts only with electron-rich molecules such as olefins, eneamines, some phenols and polycyclic aromatics. Rate constants summarized in Table 20 show that of the structures listed only branched alkenes react fast enough with ozone for this reaction to compete with oxidation by HO• radical. A useful summary of specific rate constants for ozone oxidations in the gas phase is found in Hendry and Kenley's report (1979).

Huie and Herron (1974) were able to correlate rate constants, k_{O_3}, for gas-phase oxidations with ionization potentials for olefins. As expected the value of k_{O_3} increases with increasing ease of ionization. We are aware of no other SRC for ozone reactions in the atmosphere.

26.2 Limitations of Methods

Oxidation processes illustrate the power of SARs to quickly distinguish between chemicals that are likely to oxidize in water or air and those that will not and with a high degree of reliability and accuracy. Part of this reliability comes from having a good theoretical understanding of the processes and part comes from having fairly extensive data bases.

Oxidation in water occurs by reactions of free radicals or singlet oxygen with specific reactive sites in the molecule. Both oxidants are very selective in their reactions, and most chemicals oxidize too slowly in water for this process to be a dominant one. Those relatively few structural features that are easily oxidized are readily recognized and can be selected for either additional estimates or measurements; examples are phenols and aromatic amines. Good SARs are available for many of these reactions in organic solvents, and our evaluation indicates that these reactivity patterns hold for water. Oxidations in air occur by reaction with HO radical, a very reactive and nonselective radical. Most chemicals will oxidize rapidly in air, and this process is the dominant one for loss of most organic structure. As in oxidation in water, the structures that are especially unreactive toward HO • are easy to recognize and select for special consideration. In both water and air less than about 10% of the chemicals fall into the very reactive or unreactive class.

We can readily show from data in the preceding section that radical oxidation ($RO_2\cdot$) in water must have a second-order rate constant of 1×10^3 M^{-1} s^{-1} in order that the chemical have a half-life < 200 h; similar arguments lead to a value of 1×10^6 M^{-1} s^{-1} for singlet oxygen reactions and 3×10^8 M^{-1} s^{-1} for HO oxidations.

Two principal sources of uncertainty in oxidation reactions are the value of the second-order rate constant for the specific process

$$\text{Rate} = k_{ox}(Ox)(C)$$

and the value of the concentration of oxidant (Ox) averaged over some time period. Estimation methods for k_{ox} are quite reliable and fairly accurate; that is, we know with a high degree of confidence that a value of k_{ox} is above or below some limit and can estimate the actual value within a factor of two to five for most ordinary kinds of molecular structures. Of greater uncertainty is the oxidant concentration in water or air. In water the concentrations of free radicals or singlet oxygen that are believed to be most important for effecting oxidation are known only within a factor of ten averaged over several diurnal cycles in spring to summer season. This uncertainty makes the overall estimate of the first-order process constant $k_{ox}(Ox)$ uncertain by as much as a factor of 100. Estimates for HO radical concentrations in air probably are more accurate and have received much more attention so that estimated process constants probably have uncertainty limits of a factor of ten, again averaged over the diurnal cycle, but adjustable for seasonal variations.

26.3 Recommendations

SARs and rules for oxidation by several oxidizing species need to be tested to determine limitations of the method. Because oxidation by OH• in air is an important process for many organic chemical, a larger data base for OH• radical reaction needs to be obtained to further develop this important SAR.

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27 BIOTRANSFORMATION RATE CONSTANT, k_{b2}

The biotransformation rate constant for initial transformation of a chemical is usually of major interest for evalauting the fate of a chemical in an environment. Although there is a fair amount of information on biotransformation of organic chemicals, most of the data have been obtained under different experimental conditions and are difficult to compare for use in establishing SARs. The estimation of biotransformation rate constants also is complicated by the situation that no generally accepted procedure for measuring these rate constants is available; this is due in part to the complex nature of the process and the lack of a quantitative understanding as to how various factors (e.g., pH, nutrients, type of organisms) influence the biotransformation rates. Most of the data available are observed first-order rate constants, k_{b1}, an approach that does not distinguish between the inherent reactivity of the chemical and the experimental parameters (e.g., organism population, pH) that also contribute to the overall rate of loss of the chemical. Paris et al. (1981) have suggested that biotransformation rates of a chemical at low concentrations, C, can be expressed as a second-order process

$$\frac{-dc}{dt} = k_{b2}[B][C]$$

where [B] is the concentration of bacteria (in organisms/liter) and k_{b2} is a second-order rate constant. This approach is most useful for developing SARs for biotransformation because k_{b2} can then be considered as reflecting the reactivity of the chemical and subject to studies to determine the effect of structural changes on this rate constant. This is the rate constant used in the EXAMs model.

27.1 Estimation Methods

Lyman et al. (1982) have discussed the complexity of estimating biotransformation rates and have described the organisms and populations that may be present in different experimental or environmental situations relevant to the measurement or estimation of biotransformation rates. They also show discrete pathways by which biotransformation may occur and list valuable rules for assessing the effect of structure changes on biotransformation rates. Rules for evaluating the effect of structure on biotransformation have also been discussed by other authors. Application of these rules requires expertise in biotransformation processes and is subject to large and indeterminate error.

As discussed in other parts of this report, development and application of SARs requires that a common mechanism be operating for all chemicals treated by a SAR. Because organisms have a potential capacity for effecting different transformation pathways, SARs for biotransformation must be developed and interpreted with some caution, preferrably with identification of the primary transformation products. This is usually difficult, however, because the products usually are more biodegradable than starting material. Limiting biotransformation SARs to a particular class of chemicals is an obvious approach to minimizing the problems of multiple pathways, and this approach has been applied to the reactions of esters, in which it is assumed that biologically mediated hydrolysis is the dominant process. As shown below, these studies indicate that sorption phenomena related to octanol/water partition coefficients as well as reactivity are important in the biotransformation process.

Wolfe et al. (1980) have found that second-order rate constants for biotransformation of two sets of esters were correlated with the second-order rate constants for base-promoted hydrolysis, k_B. They also found that inclusion of K_{ow} term in the correlation slightly improved the correlation, but that the correlation with k_B dominated the relationship. These results imply that the rate-determining step of biotransformation occurs by a mechanism in which enzymatic attack on the ester occurs by a nucleophilic process similar to that that occurs by hydroxide ion (Gould, 1959). In apparent contrast with these results, Urushigawa and Yonezawa (1979) have reported that the first-order biotransformation rates of a set of phthalate esters were correlated with their retention times (Rt) in a reverse-phase partition chromatography system; these authors showed that Rt was also correlated with K_{ow} values. The authors did note however, that three phthalate esters (specifically the diethyl, dibutyl, and diheptyl esters) did not fit the correlation and that they are much more reactive than the other esters based on other studies. Because the studies of Urushigawa and Yonezawa were performed using organisms from sewage sludge, whereas the studies of Wolfe et al. were peformed using acclimated systems from natural waters, the two sets of data cannot be directly compared. However, the results from the two papers do show that use of either reactivity or K_{ow} values alone to correlate the biotransformation rate constants is insufficient and that the predictive ability of the correlation equations is severely limited, if useful at all. The fact that the correlations were found is promising, however, and much more work is required to develop and test such relationships.

27.2 Limitations of Methods

There are several rules that can be used with some confidence by persons with expertise in biotransformation, and estimates of the biotransformation half-lives can be made by these persons for environments of specific concern to EPA. As discussed above, the several quantitative correlations available for biotransformation indicate that the SAR approach is feasible for correlating biotransformation rate constants, but that much more information on the specific biotransformation processes and supporting data is required before the approach is useful for predicting these rate constants for new chemicals.

27.3 Recommendations

Carefully designed studies to develop SARs for biotransformation processes need to be performed.

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28 DEVELOPMENT OF A COMPUTERIZED SAR SYSTEM

28.1 Introduction

Incorporation of SARs and other estimation methods in a computer format is a logical and necessary step to gain full advantage of these methodologies for simplifying fate assessments. EPA-OTS has begun a preliminary effort in this direction in computerizing some portions of the book by Lyman et al. (1982). As it now exists, this system is actually a directory for finding suitable methods in external sources (usually the Lyman book), and then for facilitating a calculation of a property or constant using a selected SAR, PRC, or other equation. Successful use of the system requires considerable judgement and expertise as well as some calculations external to the computer system. Nevertheless, this effort is an important step toward bringing a large amount of knowledge into the fate assessment process which is not available in current data base systems. The long-term objectives for a fully computerized estimation system should include the following features:

- Multiple user capability
- Multiple levels (screening and advanced assessments)
- Flexibility and completeness
- Self-contained for providing limited or approximate values
- Data bases for detailed estimates
- Compatibility with existing systems
- User friendly
- Easily modified and extended
- Readily critiqued.

Some of these features are self-evident and others require discussions among the system users, computer scientists, and the research scientists that generate the data for the SARs and PRCs. Undoubtedly, other features of the system will be recognized and addressed as the computerized system is developed and put into use.

A critical feature of a practical computerized SAR system is the development of structure-search routines that are tailored to the individual processes for which data estimations are made. Design of these search systems should incorporate the kind of expertise employed by scientists when they make assessments without the assistance of computer systems. The successful incorporation of expert knowledge and decision-making criteria into computer format is exemplified by systems such as the PROSPECTOR geological program developed at SRI for locating mineral deposits, the DENDRAL program developed at Stanford University for analyzing mass spectral data, and other medical and chemical programs developed under the rubric of artificial intelligence.

The incorporation of estimation methods into a computerized system will require interaction of various disciplines and application and adaptation of existing programming capability as well as development of new systems. For the philosophy used in developing the systems, we believe that in the short term existing SARs must be used and that qualitative SARs can be extracted from data bases for use with the quantitative relationships. We also believe that for the screening level estimates, no information external to the system (except for molecular structure) is needed to effect a series of estimates for all important transformaton and transport processes. For some processes, notably photolysis and biotransformation, few SARs exist, therefore we must resort to limiting values and depend on intercomparison of all process constants as a basis for decision as to where to focus additional time and resources. Currently, in some estimation methods only laboratory measurements can provide the needed accuracy of data for some processes, but the investigator can then be confident that only the necessary processes are being carried forward. Because transport and transformation processes rely on fundamentally different properties, they may be developed as separate systems, which are discussed below.

Transport Processes

If the user wishes to estimate data for the sorption or volatilization of a chemical, an appropriate sequence of calculations could be performed in an interactive procedure. Flow charts for estimating sorption or volatilization processes are shown in Figures 28.1(a) and 28.1(b), respectively. The values of K_{oc}, S_w, or k_{vc}, listed on the right of the figures, are usually required for a fate assessment. Each value on the left can be used to estimate the value on the right using an SAR, PRC, or estimation equation.

Figure 28.1(a) shows that values of K_{oc} and S_w can be calculated from K_{ow} values. Calculating K_{ow} values from K_{oc} and S_w values is probably not useful except as a check on a K_{ow} value calculated using the FRAGMENT approach, and then only if the K_{oc} or S_w, value is reliable.

Figure 28.1(b) shows that the volatilization rate constant for a chemical, k_{vc}, can be calculated from physical properties estimated by SAR methods. These calculations are discussed in detail in Sections 15 through 17. Because the calculation of k_{vc} is somewhat tedious and prone to calculation error and requires selection of environmental conditions by the user, estimations of k_{vc} appear to be ideal for an computer interactive system with default values available for the environmental parameters of depth, temperature, and mass transfer coefficients for water and oxygen in ponds/lakes or rivers.

In the incorporation of the various estimation methods into an SAR system, it will be necessary to select some SARs or PRCs over others, especially if the system is to take a tiered approach or to have an option of not being interactive with the user. Thus, certain PRCs for K_{ow}-K_{oc} or K_{ow}-S_w will have to be chosen; the recommended equations are given in Sections 8 and 10, respectively. Similarly, estimation of diffusion coefficients for estimating volatilization rate constants will require decisions between the simplicity of the use of the molecular weight approach or the more accurate estimation methods using the SARs (see Section 15).

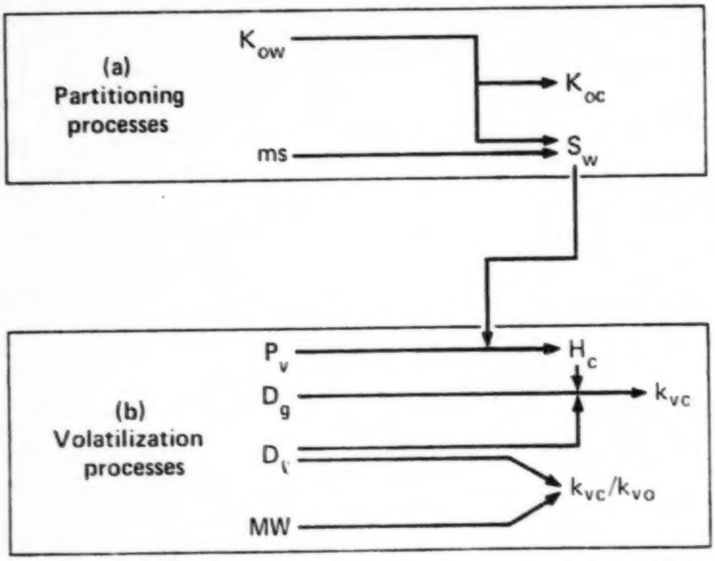
(a)
Partitioning
processes
K_{ow}
K_{oc}
ms
S_w
(b)
Volatilization
processes
P_v
H_c
D_g
k_{vc}
D_l
k_{vc}/k_{vo}
MW

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Figure 28.1 Flow chart for estimating (a) partitioning and (b) volatilization processes.

28.3 Transformation Processes

Kinetic or equilibrium constants required for evaluating transformations reactions include those for the processes of hydrolysis, oxidation, photolysis, dissociation equilibria, and biotransformation, and an SAR computer program needs to recognize both classes and subclasses of structures that will undergo each kind of process. The program would then provide the best estimate for each process. As discussed in Sections 23 and 24, SARs for photolysis are extremely limited, but if the user can provide spectral data through an appropriate SAR (see Section 25), then a maximum value of k_p (where $\phi = 1$) can be computed for a reference latitude and season and compared with other competing transformation and transport processes.

The initial efforts in implementing a useful screening SAR program are to select simple, useful, and abundant SARs for conversion to computerized forms. Some of these forms are presented in Sections 5 through 27 and SARs for hydrolysis are discussed by Mill et al. (1982); however, no actual computerization of these SARs has been done thus far. Both oxidation and hydrolysis have good data bases which are adequate for screening level SARs, and their incorporation into a computerized format will be applicable to a wide range of chemicals.

In designing formats to be incorporated into a computerized SAR system, it is important to remember that the effectiveness (in terms of practicality, cost, and accuracy) of screening-level programs depends in large part on the design of the reaction center search routines. If a routine attempts too fine a subdivision of reaction centers, the program becomes too complicated and slow; too little discrimination between reaction centers will produce less reliable estimates. Thus, the degree of subdivision detail must be a balance of what the system users require in terms of accuracy and speed, and to a certain extent on the reaction processes in question. For instance, substructure searches to estimate oxidation rate constants can be relatively crude because oxidations are either very fast (as for HO reactions) or very slow (as wth RO_2

oxidations.) On the other hand, hydrolysis rates can be very sensitive to structural variations, and refined structure searches are needed to avoid significant errors in estimated rate constants. For example, the presence of a hydrogen on the nitrogen of a carbamate has a large effect on the base-promoted rate constant, k_B (see Section 22).

In conclusion, successful computerization of SARs as well as PRCs and other estimation methods requires careful and cooperative efforts of persons with diverse expertise.

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